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A General Mechanism for Negative Capacitance Phenomena

A Dissertation

Presented to

the Faculty of the Department of Physics

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

By

Jason Brian Shulman

December 2009

A General Mechanism for Negative Capacitance Phenomena

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ABSTRACT

Negative capacitance (NC) is a relatively unknown, yet common, phenomenon that is found in a wide variety of materials and devices spanning the major branches of science. The microscopic mechanisms governing NC in these systems are, naturally, as varied as the materials themselves. However, they do share several common features. NC arises in the presence of a *dc* bias, while the materials themselves are nonlinear and possess strong dispersion. The current study focuses on NC in an electrorheological fluid composed of urea coated $\text{Ba}_{0.8}(\text{Rb})_{0.4}\text{TiO}(\text{C}_2\text{O}_4)_2$ nanoparticles dispersed in silicone oil. The NC of the fluid is plasma-like in nature and related to the nonlinearity of the fluid's conductivity. A general mechanism, describing the NC of the fluid as well as other materials, has been developed by exploiting the common features associated with NC. The mechanism demonstrates that NC arises from *dc/ac* signal mixing across a nonlinear conductor.

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Chapter 1: Introduction

The subject of this work, negative capacitance (NC), is a common, yet somewhat unknown, phenomenon that arises in many areas of science. Before delving into a discussion of such a specialized topic, it might be useful to briefly introduce the physical foundations and basic mathematical relationships of general dielectric phenomena as well as typical dielectric behavior, or that which is generally observed in experiments. This will be presented in the following sections. Next, the existing body of work pertaining to NC will be summarized. Unfortunately, many of the previous investigations into NC have typically been restricted to the individual material in question. The study of NC as a phenomenon in and of itself, consequently, has been rather limited. The present work is an attempt to break from this trend by offering insight into NC in general and not simply one material. This will be accomplished by extracting features common to many instances of NC from the system under study in this work, which is based on an electrorheological (ER) fluid. Thus, this introductory chapter would be incomplete without including a discussion of the ER effect and the particular fluid examined during the course of this project. Finally, the chapter will conclude with a short overture, which will summarize the body of work that is to follow.

1.1 Physical and Mathematical Foundations

This section will review the fundamental concepts of dielectric behavior. In no way comprehensive, its purpose is to simply provide a framework in order for the experimental results to be put into context.

Upon application of an electric field, a dielectric material will become polarized. The nature of the polarization depends on the microscopic content of the material. However, in general, the relationship between the frequency dependent polarization (P) and total field (E) is, in the case of a linear dielectric,

$$\tilde{P}(\omega) = \epsilon_o \tilde{\chi}(\omega) \tilde{E}(\omega). \quad (1.1)$$

The parameter describing the polarization of the material, $\tilde{\chi}(\omega) = \chi'(\omega) - i\chi''(\omega)$, is referred to as the susceptibility, and ϵ_o is the permittivity of free space. It is a complex function of frequency, and thus, contains information about the amplitude as well as the phase of the polarization [1]. Another useful relationship in electrodynamics describes the electric displacement,

$$\tilde{D}(\omega) = \epsilon_o \tilde{E}(\omega) + \tilde{P}(\omega). \quad (1.2)$$

The total current density generated by the electric field will be

$$J = \sigma_o E + \frac{\partial D}{\partial t}. \quad (1.3)$$

The first term represents the contribution from free charges within the material and is not associated with polarization. The second term is the displacement current. In the frequency domain, equation (1.3) can be written as

$$\tilde{J}(\omega) = \sigma_o \tilde{E}(\omega) + i\omega \tilde{D}(\omega) \quad (1.4)$$

since the Fourier transform of a derivative can be conveniently simplified to

$$FT\left[\frac{\partial D}{\partial t}\right] = i\omega \tilde{D}(\omega). \text{ Substituting (1.1) and (1.2) into equation (1.4) results in}$$

$$\tilde{J}(\omega) = \left\{ \left[\sigma_o + \varepsilon_o \omega \chi''(\omega) \right] + i\omega \varepsilon_o \left[1 + \chi'(\omega) \right] \right\} \tilde{E}(\omega). \quad (1.5)$$

It is clear that the real part of the susceptibility describes the off-phase current. As such, it is not associated with power loss. On the other hand, the imaginary part of the susceptibility yields a current in phase with the field and does contribute to power loss. χ'' is, therefore, referred to as the dielectric loss.

The frequency domain response of a material can be written in terms of a dielectric permittivity, $\tilde{\varepsilon}_p(\omega)$ [1], which is defined by the equation,

$$\tilde{D}(\omega) = \tilde{\varepsilon}_p(\omega) \tilde{E}(\omega). \quad (1.6)$$

By writing the current density from equation (1.5) in the form $\tilde{J}(\omega) = i\omega \tilde{\varepsilon}_p(\omega) \tilde{E}(\omega)$, one can see that

$$\tilde{\varepsilon}_p(\omega) = \varepsilon_o \left(1 + \chi'(\omega) \right) - i\varepsilon_o \left(\chi''(\omega) + \frac{\sigma_o}{\varepsilon_o \omega} \right). \quad (1.7)$$

This demonstrates that the dielectric loss measured in an experiment necessarily includes any contribution from free charges in the system. This is reasonable since instruments typically measure overall current in the system. They cannot differentiate between effects due to polarization and those associated with free charge.

Throughout this report, susceptibility and polarization data will not be provided explicitly since it is often more convenient to present the directly measured capacitance

or dielectric constant $\left(\frac{\epsilon'_p}{\epsilon_o}\right)$ of the material. However, the calculation of susceptibility and polarization is straightforward with equations (1.1) and (1.7) as well as other relationships which will be defined in the following chapter.

1.2 General Dielectric Behavior

The experimental results obtained throughout this work will be presented in Chapter 3. However, it should be instructive to discuss what is generally considered “typical” dielectric behavior of condensed matter systems in order to demonstrate what one might expect from such experiments. A simple, yet powerful model describing dielectric polarization will be used to illustrate this behavior. The model, which consists of a charge $-e$ with mass m that is harmonically bound, with a force constant k and damping parameter γ , to an equilibrium position, has been described in detail by Jonscher [1] and Jackson [2]. The discussion below closely follows these two works.

The equation of motion for the charge in the presence of an electric field $E(x, t)$ is

$$m\ddot{x} + m\gamma\dot{x} + kx = -eE(x, t), \quad (1.8)$$

where x denotes the displacement from equilibrium. In writing (1.8), a few assumptions have been made. First, it has been assumed that the local field is equal to the applied field. Also, the displacements must be small enough so that the electric field can be evaluated at the average position of the charge. If there are N identical, non-interacting

charges per volume, the polarization of the system will be $P = -eNx$. Let the electric field be a harmonic function of time, $E = E_o e^{i\omega t}$. Then, equation (1.8) can be solved for x and the polarization will be $\tilde{P} = \frac{e^2 N}{m} (\omega_o^2 - \omega^2 + i\omega\gamma)^{-1} E$, where $\omega_o = \sqrt{k/m}$ is the natural frequency of oscillation of the charge in the absence of damping. The susceptibility, from (1.1), is

$$\tilde{\chi}(\omega) = \frac{\omega_p^2}{(\omega_o^2 - \omega^2 + i\omega\gamma)}, \quad (1.9)$$

where $\omega_p^2 = \frac{e^2 N}{\epsilon_o m}$ is the square of what is referred to as the plasma frequency. Equation (1.9) gives rise to anomalous dispersion and resonant absorption discussed in many physics textbooks. For the present, however, one only needs to examine two limiting cases of the model.

Case 1: An inertialess system

If one minimizes the role of inertia in (1.8), the model reduces to a system dominated by damping effects. This results in a simplified Debye model that describes the response of a collection of dipoles. In order to achieve an inertialess system, one must resort to some minor mathematical manipulation. First, one sets $m = 0$ while choosing the damping parameter such that

$$\frac{m\gamma}{k} \equiv \tau \quad (1.10)$$

remains finite. Note that $m\gamma$ is finite so that γ tends toward infinity. If one applies this limit to equation (1.9), the real and imaginary parts of the susceptibility $\{\tilde{\chi}(\omega) = \chi'(\omega) - i\chi''(\omega)\}$ become

$$\chi'(\omega) = \left(\frac{e^2 N}{\epsilon_o k} \right) \frac{1}{1 + \omega^2 \tau^2} \quad (1.11)$$

$$\chi''(\omega) = \left(\frac{e^2 N}{\epsilon_o k} \right) \frac{\omega \tau}{1 + \omega^2 \tau^2} . \quad (1.12)$$

Equations (1.11) and (1.12) represent the susceptibility of a viscous system in which inertial effects are minimized. They have the characteristic Debye dispersion, which is shown in Figure 1.1. This is the “typical” dielectric behavior that was mentioned previously. However, in reality, few materials actually exhibit Debye behavior. Researchers sometimes erroneously attempt to describe non-Debye data by a series of Debye dispersions with a distribution of time constants [3, 4].

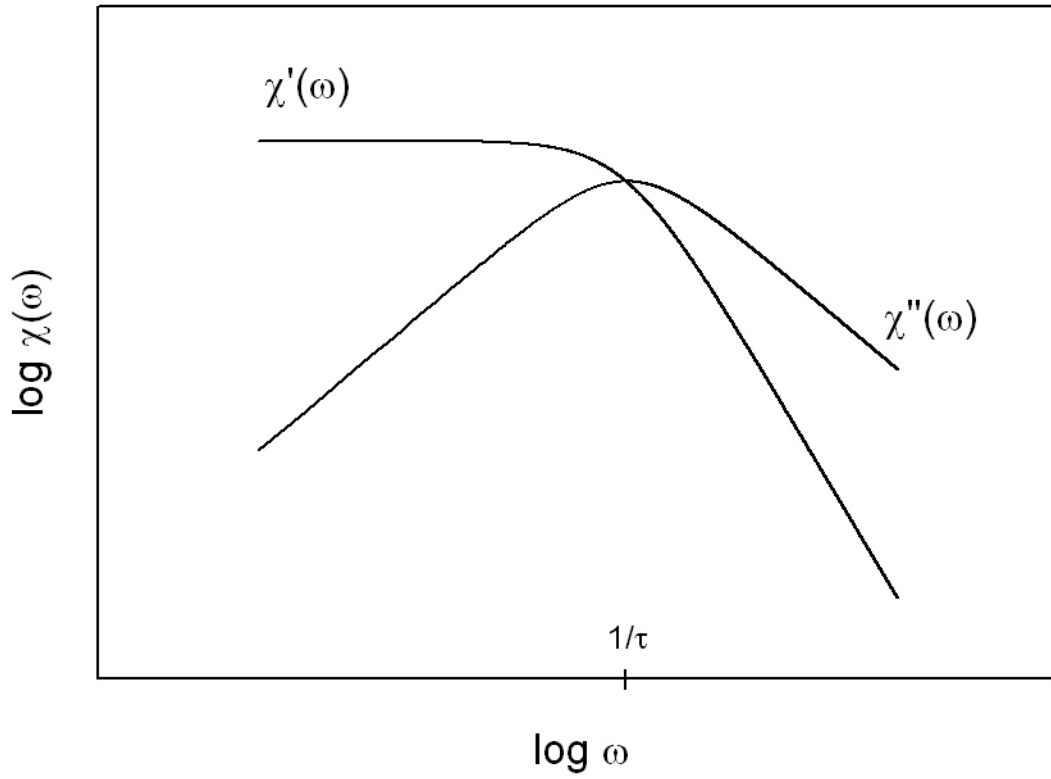


Figure 1.1. Debye dispersion given by equations (1.11) and (1.12). The loss peak in $\chi''(\omega)$ occurs at $1/\tau$.

Case 2: Free carriers

The response of a system of free carriers with collisions can be modeled by removing the restoring force in equation (1.8), *i.e.*, setting $k = \omega_o = 0$ and, thus, unbinding the charge from its equilibrium position. This results in a collection of charge free to move through the material but subject to collisions determined by γ . In other

words, the material is now a damped plasma. The solution is attained by simply making the same substitution in equation (1.9),

$$\chi'(\omega) = \frac{-\omega_p^2}{\omega^2 + \gamma^2}, \quad (1.13)$$

$$\chi''(\omega) = \frac{\omega_p^2 \gamma}{\omega(\omega^2 + \gamma^2)}. \quad (1.14)$$

The total permittivity ($\tilde{\varepsilon}_p = \varepsilon_0 + \varepsilon_0 \tilde{\chi}$) of such a material will include contributions from other polarizing mechanisms as well as the contribution from free space, resulting in

$$\varepsilon'_p(\omega) = \varepsilon_\infty - \varepsilon_0 \frac{\omega_p^2}{\omega^2 + \gamma^2}. \quad (1.15)$$

Thus, the permittivity can be negative at sufficiently low frequencies if

$$\frac{\varepsilon_0 \omega_p^2}{\gamma^2} > \varepsilon_\infty. \quad (1.16)$$

A consequence of (1.15) and (1.16), which is relevant to this work, is that the static permittivity of a plasma is negative,

$$\varepsilon'_p(\omega=0) \cong \frac{-\varepsilon_0 \omega_p^2}{\gamma^2}. \quad (1.17)$$

This important aspect will be discussed in subsequent chapters.

The conductivity can be calculated by equating two equations for the current density, $J = \tilde{\sigma}E = i\omega\tilde{\varepsilon}_p(\omega)E$, so that

$$\tilde{\sigma} = i\omega\tilde{\varepsilon}_p \quad (1.18)$$

or

$$\sigma' + i\sigma'' = i\omega(\varepsilon'_p - i\varepsilon''_p). \quad (1.19)$$

From equation (1.14), the conductivity (real part) can then be written as

$$\sigma'(\omega) = \varepsilon_o \frac{\omega_p^2 \gamma}{(\omega^2 + \gamma^2)}. \quad (1.20)$$

A graph of $\varepsilon'_p(\omega)$ and $\sigma'(\omega)$ for a damped plasma is displayed in Figure 1.2.

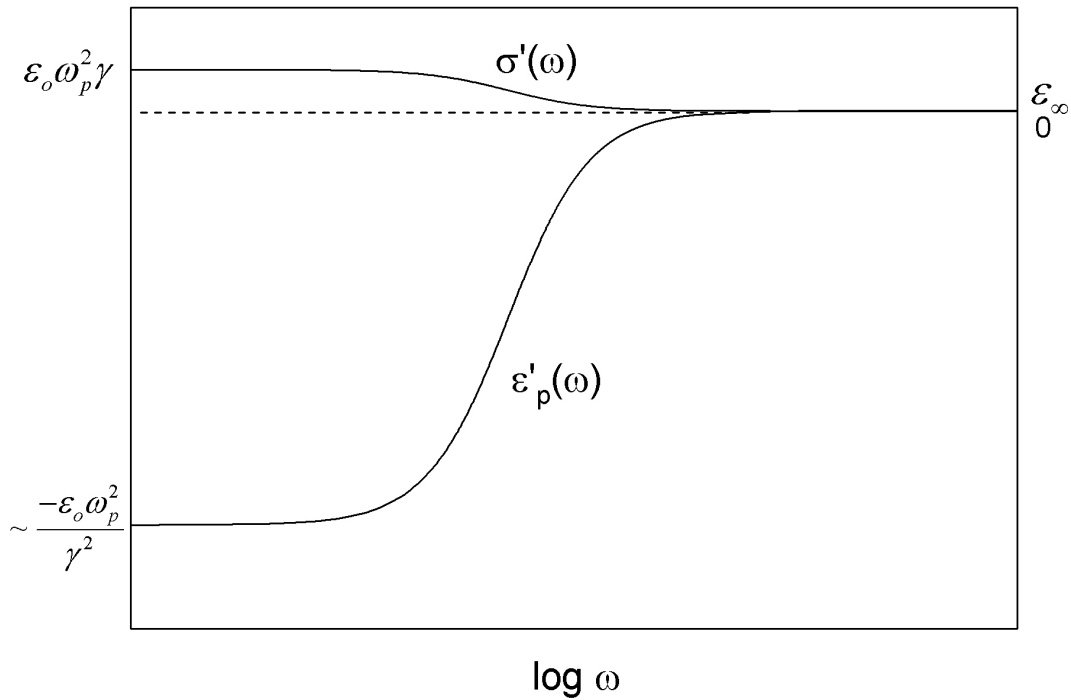


Figure 1.2. The dielectric response of a damped plasma. The high frequency limits of the permittivity and the conductivity are ε_∞ and 0 , respectively. At low frequencies the permittivity becomes strongly negative.

The difference between the two cases is clear. The susceptibilities for the heavily damped (Debye) material are positive. In the plasma, the inertial effects cause the real part of the susceptibility to become negative. Interestingly, aside from the sign

difference, the dispersions of $\chi'(\omega)$ for the two cases are identical. The negative susceptibility of the plasma can cause the dielectric constant to become negative at low frequencies, particularly in the case of small damping.

As previously stated, an exact Debye dispersion is almost never observed in actual materials. Instead one finds the almost ubiquitous universal dielectric response (UDR) of disordered solids [1, 5, 6]. As stated by Jonscher [5],

“...the dielectric relaxation of virtually all solids follows fractional power laws in both time and frequency, with a range of exponents which are capable of describing all experimentally observed behaviours.”

The relaxation is necessarily associated with some type of disorder within the material since there can be no relaxation in a perfectly ordered system. In the extreme disorder limit, the conductivity is independent of the details of the disorder, which can be thought of as a random RC network with a distribution of the values of R and C. The conductivity, in this case, is governed by percolation through the network and is characterized by a transition from a constant value at low frequencies to $\sigma(\omega) \propto \omega^n$ with $0.6 < n < 1$ [6]. The dielectric constant of such a system demonstrates low frequency dispersion (LFD) due to the power law nature of the response function [1, 3-5].

The materials studied during the course of the project reside in this limit of extreme disorder. Thus, relevance of UDR to the present work is expected.

1.3 Negative Capacitance

With the exception of the damped plasma, the capacitance of the situations described above is strictly positive since $C' \propto \varepsilon'_p$ and the constant of proportionality is a positive geometric factor. Moreover, in the case of the plasma, the damping parameter is often large, *e.g.*, $\gg 10^9 \text{ s}^{-1}$ for metals [7]. This renders the negative term in the permittivity (equation (1.15)) rather small and the inequality in (1.16) unlikely to be satisfied. Additionally, from an experimental point of view, in such a situation the conductivity (1.20) will be the dominant factor in the measured admittance and the off-phase component will not be resolved. Therefore, in many circumstances, the measured capacitance of a damped plasma is positive or negligible.

Yet, as stated in the introductory paragraph, NC is quite common. It has been observed in samples as different as crystalline and amorphous semiconductor devices, organic compounds, composite/nano materials, electrochemical cells, geological samples, biological membranes, and even moist surfaces. Furthermore, it has been shown that NCs can originate at interfaces as well as in the bulk of the materials.

NC has been observed for decades, yet despite being so common and wide ranging, it has only recently started to gain recognition. It is believed that this is due to many early observations going unreported as researchers attributed such odd and puzzling effects to experimental error or poor instrument calibration. When NC was actually discussed, it was often referred to as “anomalous” or “abnormal” capacitance [8]. One example, indicative of the negative prevailing attitude towards NC, is from the

relatively recent technical report [9] supplied by Solartron Analytical, a leading provider of spectroscopy instrumentation. The report describes analyses of NC as having “no physical meaning.” Such a statement might be extreme, but it is true that theoretical work has not maintained a pace comparable to that of experimental efforts. Many theoretical investigations have been based on electrostatic charge redistribution within the material. A capacitance calculation of this type, however, is incorrect when the NC is accompanied by a large conduction current, which is often the case [8]. With the sheer volume of NC observances under vastly different experimental situations, in both the time and frequency domains, it is now, fortunately, undeniable that NC is an actual phenomenon and not due to an experimental error that arises during measurement or the subsequent analysis.

The majority of the NC investigations thus far have focused on a single material or device. As such, they are of limited value for the present, that is, in an introduction to NC phenomena. General investigations into NC will indeed be described below, but preceding this, two examples of NC specific to their individual systems will be briefly discussed. The purpose is twofold. First, such a presentation will highlight the diverse nature of the systems exhibiting NC. Second, it will also serve to demonstrate that such different materials can have very similar manifestations of NC.

The first example [10] is a heterojunction formed by depositing $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSMO) on a Nb-doped SrTiO_3 (SNT0) substrate. LSMO and SNT0 are *p*-type and *n*-type semiconductors, respectively. The observation of NC in such structures is rather unusual considering it is rarely found in *p-n* junctions, especially in contrast to Schottky diodes, which often exhibit NC. Figure 1.3a shows the measured capacitance of the

junction plotted against frequency for several applied biases. With a bias ≤ 0 , the capacitance is positive across the entire frequency range. However, upon application of a positive bias, which is defined as current flow from SNT0 to LSMO, the capacitance becomes negative at low frequencies while suffering only minor deviations from the zero bias value at high frequencies. The authors of reference 10 attribute the NC in the junction to delayed hopping between localized interfacial traps. The delay is responsible for the current lagging behind the applied field, resulting in a $C < 0$. Furthermore, it was shown that the data can be described as arising from two competing capacitive contributions, the delayed hopping (negative contribution) and a Maxwell-Wagner process (positive contribution), which is responsible for the increase in the low frequency capacitance at negative biases.

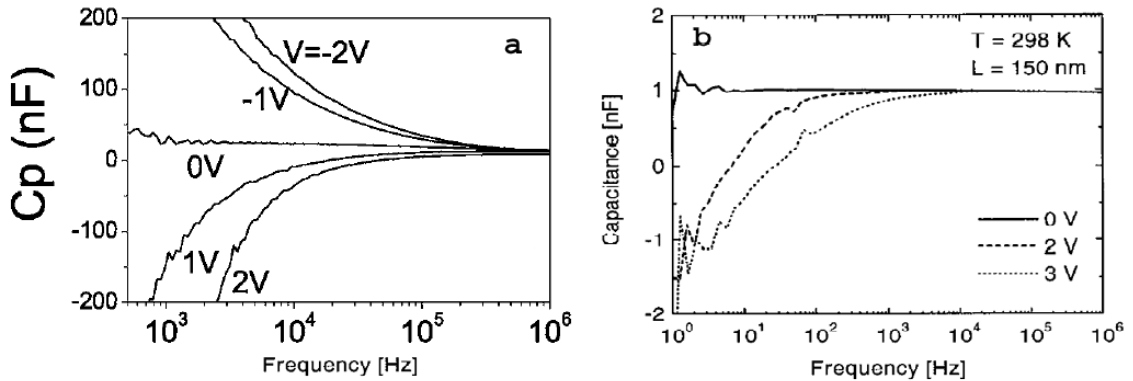


Figure 1.3. From Refs. 10 and 11. Frequency dependent capacitance of a heterojunction (a) and PLED (b) at various biases. In spite of the very different physics governing these devices, the dispersions of the capacitances are rather similar in that they are positive and relatively flat at high frequencies but become strongly negative at low frequencies. Additionally, the NC only exists in the presence of a nonzero bias. Such properties are common among the various instances of NC.

Negative capacitance, similar to that of the heterojunction, was found to arise in a polymer LED (PLED) [11]. This is not an isolated instance as NC is fairly common in organic and polymer LEDs. In this case, the polymer is poly (*p*-phenylene vinylene) (PPV). It was shown that electrons and holes each provide their own contribution to the NC in PPV and that the contributions were separated in frequency. The NC in the device was attributed to the delayed response of space charge under a changing field. The delay results from a finite transit time of the carrier as it moves into the device. From Figure 1.3b, it is clear that the NC that arises in the PPV has a similar dispersion to the heterojunction. A strongly dispersive low frequency NC, which appears only in the presence of a *dc* bias, is common. Indeed, the materials studied during the course of this project have similar capacitive properties. The fact that many different systems, operating under different physical processes, have similar manifestations of NC is highly unusual. This puzzle will be addressed in Chapter 4.

Investigations into NC as a general phenomenon has been rather limited. Penin [12] has theoretically examined NC in barrier-free semiconductors. It was proposed that NC can arise in systems exhibiting inertial conductivity, *e.g.*, Drude behavior as in case 2 above and impact ionization of impurity atoms, if the reactive component of the current exceeds the displacement current. Such a situation results in a permittivity and conductivity described by equations (1.15) and (1.20) as well as Figure 1.2 if the inequality (1.16) holds.

Jonscher's collection of NC publications, which resulted from a campaign to legitimize the subject, should be credited for stimulating interest in NC. Interestingly, he was the developer of the aforementioned concept of UDR. His vast experimental

experience in the study of the dielectric properties of materials resulted, not only in the discovery of UDR, but also in the recognition of the pervasiveness of NC in these materials. Jonscher suggested that, while NC is difficult to envision in the commonly used frequency domain, the time domain offers a physically intuitive environment for study [5, 13]. In order to motivate such a claim, he noted the association of low frequency dispersion, which arises in UDR systems in the limit of extreme disorder, with a slowly decaying current in the time domain after a step excitation. In other words, a current that decreases slowly in time is mathematically associated to a positive dispersive admittance in the frequency domain. It was supposed that a current increasing in time would correspond to negative dispersive capacitance. To test such an idea, time dependent currents were postulated and subjected to numerical Fourier transforms in order to obtain their corresponding admittances [13]. Specifically, currents of the form

$$\begin{aligned} I(t) &= t^{-n} & t_1 < t < t_2 & & n \ll 1 \\ I(t) &= t^m e^{\frac{-t}{\tau}} & t > t_2 & & m \ll 1, \quad \tau \gg t_2 \end{aligned} \quad (1.21)$$

were supposed with various values of m and n . The inclusion of the exponential factor for times larger than t_2 ensures the eventual decay of the current at large times, *i.e.*, $I(\infty) = 0$. The currents from (1.21) and the corresponding values of the complex capacitance are reproduced in Figure 1.4. Here, $C'' = \frac{G}{\omega}$, where G is the conductance of the material. The capacitance, C' , is in fact negative in a region determined by the parameters of the current, m and n . Thus, the fundamental conclusion to Jonscher's work on general NC is that, in certain situations, a sign change in the slope of a time

dependent current is manifested as a sign change of the capacitance. Jonscher asserts that it is far easier to conceive of situations in which the current will rise within a period of time before making its final decay than it is to envision a negative capacitance in the frequency domain. Yet, the two situations are representative of a single physical process. They are inextricably linked via the Fourier transform [5].

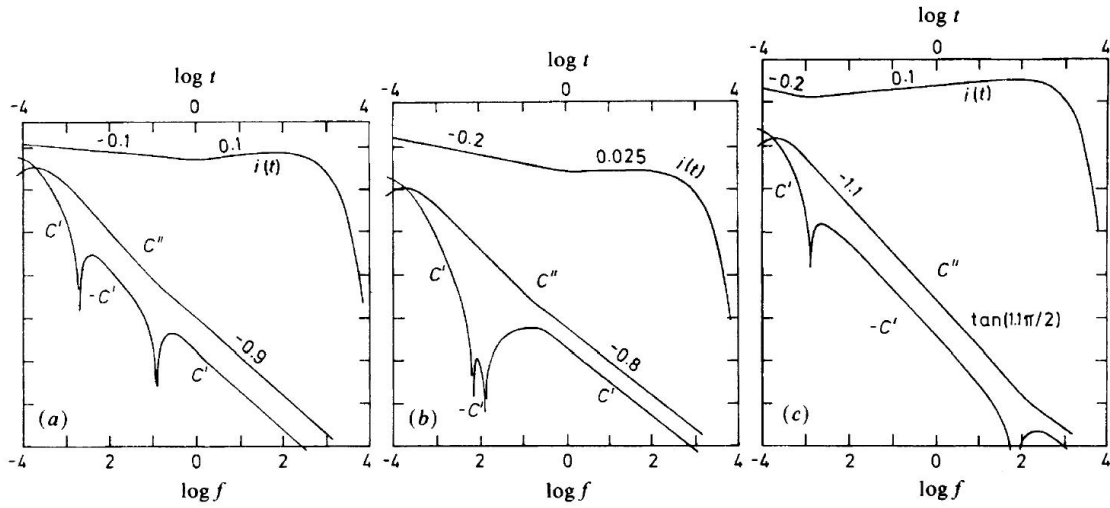


Figure 1.4. From Ref. 13. Postulated time dependent currents and their associated complex capacitances. The currents are described by equation (1.21). The parameters m and n are defined in the plots. The form of final decay is of little consequence to the result. In this case, the exponential function yields a Debye dispersion at low frequencies. The important feature to note is the NC, which is associated with a rising current.

At the time, the claim that NC was linked to a sign change in the slope of a time dependent response current was supported by very little experimental evidence. Jonscher did, however, provide an example. It was discovered that GaAs Schottky diodes [14] exhibit NC at sufficiently high forward biases. NC was absent upon application of a reverse bias. After the frequency domain measurements were complete,

one of the diodes was subjected to positive and negative step excitations, corresponding to forward and reverse biases, respectively, and the time dependent charging currents were measured. The results are shown in Figure 1.5. The current decays monotonically after application of a -1 V (reverse) bias. However, with the application of a +1 V (forward) bias, the initial decay is followed by a strong rise in the current at long times. Recall that the NC was observed only with a forward bias.

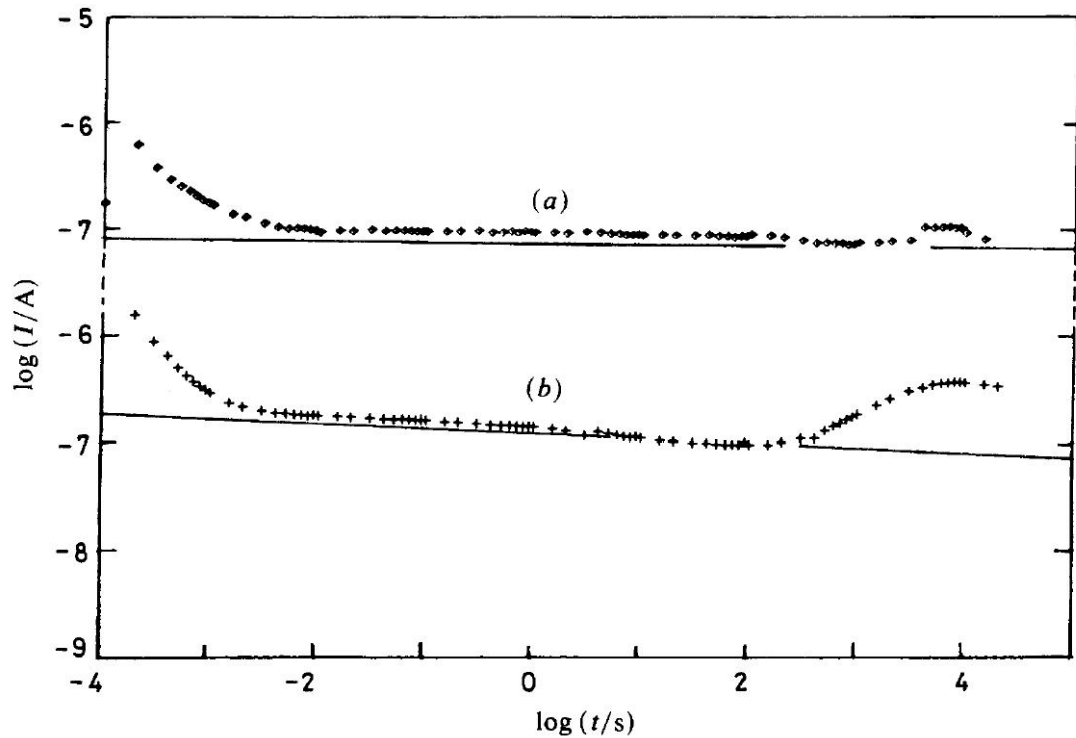


Figure 1.5. From Ref. 14. The charging currents of a GaAs Schottky diode after application of reverse bias (a) and a forward bias (b). The sharp rise at long times during forward bias is connected with NC, which was observed in frequency domain measurements.

Ershov, Jonscher, and collaborators [8] have since provided a mathematical description of Jonscher's initial concept. However, the fundamental conclusion remains the same, *i.e.*, NC is associated with nonmonotonic transient currents after a step excitation. Recently, more experimental evidence confirming such a connection has been published. Results from the current project will be supplied in Chapter 3.

1.4 The Electrorheological Effect and Fluids

The materials studied in this work are based on a colloid consisting of urea-coated $\text{Ba}_{0.8}\text{Rb}_{0.4}\text{TiO}(\text{C}_2\text{O}_4)_2$ nanoparticles suspended in silicone oil. The particles are 20-80 nm in diameter. Interest in the colloid was generated when it was discovered that the material exhibits the electrorheological (ER) effect [15]. Therefore, throughout this work, it will be referred to as the ER fluid.

ER fluids are materials whose viscosity is regulated through the application of an electric field. The simplest type of ER fluid consists of dielectric particles suspended in a nonconducting liquid. The colloid falls in this category. The particles become polarized upon application of an electric field. Dipole-dipole, and higher order, interactions result in an aggregation of the particles in the form of columns aligned parallel to the electric field [16] (see Figure 1.6). A second consequence of these interactions is an increased resistance to sheering of the fluid as the forces responsible for the aggregation resist particle displacement. This is the source of the field dependent viscosity.

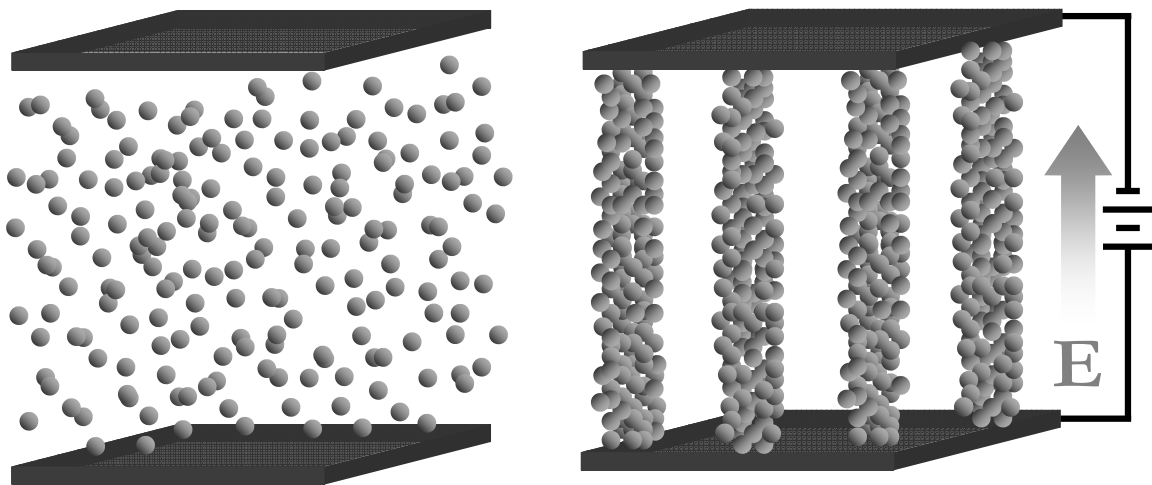


Figure 1.6. Schematic of an ER fluid in the absence and presence of an electric field. Without a field, the particles are randomly distributed in the liquid. Upon application of a field, the forces on the particles are such that they form columns. This results in an increased viscosity.

The particular fluid studied throughout this project demonstrates an unusually strong ER effect [15]. In fact, at sufficiently high fields, the fluid undergoes a liquid-solid transition. Furthermore, the material possesses a static yield stress that surpasses the theoretical upper limit.

1.5 This Work

The fluid exhibits a very strong ER effect. As will be seen in Chapter 3, it also displays NC. The current work is a study of NC in the ER fluid. However, one of the

foremost tasks undertaken upon the start of the project was to investigate any possible relationship between these two unique features of the fluid. In particular, it was to be determined if the ER effect was responsible for the NC in the fluid.

However, before presenting any discussions of the mechanism, the NC itself will be characterized and described in both the time and frequency domain. It will be shown that NC in the fluid is plasma-like in nature; *i.e.*, the admittance has a plasma-like dispersion. Furthermore, current resulting from a step excitation has a nonmonotonic time dependence, which is in accordance with Jonscher's time domain hypothesis. It will also be shown that, unlike some instances of NC, the NC of the ER fluid is associated with a negative differential dielectric constant. Measurements of the accumulated charge will indeed show that the differential polarization is negative.

Finally, a general mechanism, responsible for the NC in many different materials, will be derived. It will be shown that the mechanism correctly describes the NC of the ER fluid as well as a fuel cell. The mechanism demonstrates that the NC in many systems arises due to dispersive nonlinearity of the conductance.

1.6 Chapter References

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Chapter 2: Experimental Methods

The current chapter presents the general experimental techniques employed during the course of this project. Preparation for the experiments will first be discussed. This includes sample preparation, measurement cell construction, and practices developed to maintain sample stability. The various experimental methods will then be presented. The focus of this project has been to determine the complex impedance of the sample in question. A mathematical description of general impedance measurements will be followed by a discussion of the circuit used in our experiments. A significant variation to this technique, the *ac* I-V loop measurement, will also be discussed. This chapter will end with a brief description of our time domain experiments.

2.1 Electrorheological Fluid Preparation

An electrorheological (ER) fluid, consisting of urea-coated $\text{Ba}_{0.8}\text{Rb}_{0.4}\text{TiO}(\text{C}_2\text{O}_4)_2$ nanoparticles immersed in silicone oil, was the primary material under study during the course of this project. Detailed descriptions of the nanoparticle synthesis are provided in Refs. 1 and 2. The viscosity of the silicone oil was 10^{-2} Pa·s. The desired amounts of nanoparticles and oil were mixed in a ball milling machine for 2-6 hours at 450 rpm.

It was discovered that, over time, in the presence of a *dc* bias the nanoparticles tend to drift to the low voltage electrode. This would result in a layer of oil between the positive electrode and a dense layer of nanoparticles. Such a configuration is

problematic, not only because the material is no longer homogeneous but also due to the fact that the inhomogeneity changes with time. Additionally, this double layer configuration can be thought of as two capacitors in series. The capacitance associated with the nanoparticles is typically negative with a large magnitude while that of the oil is smaller and positive. The overall measurement of the capacitance, therefore, could be significantly shifted in the positive direction due to a small layer of oil.

Fortunately, an exact nanoparticle to oil ratio was rarely needed. The above-mentioned problem was minimized by removing the excess oil from the fluid after ball milling. To do this, Kimwipes were inserted into the fluid. Kimwipes readily absorb the oil, and the nanoparticles do not stick to them when they are removed. This results in a fluid with a minimal oil content and “close packing” of the nanoparticles.

2.2 Pellet Preparation

In addition to the ER fluid, pellets made from the nanopowder used in the ER fluid were also studied. Construction of the pellets proceeded as follows. First, two indium electrodes were created by flattening the Indium in a hydraulic press. Next, the nanopowder was inserted into the press, and the desired force was applied, yielding a dense pellet. Finally, everything was reinserted into the press in an electrode-disk-electrode configuration. The result was a solid pellet sandwiched between two thin Indium electrodes. Wires were attached to the outer faces of the electrodes using either silver epoxy or silver paste.

2.3 Measurement Cell Construction

This section will describe the construction of a typical cell used for measurements of the ER fluid. The general configuration consists of two metal electrodes which are epoxied to two support pieces. The support pieces are then epoxied together with a spacer between them to fix the gap (see Figure 2.1). Almost all fluid experiments were performed with a cell of this type or a slight variation.

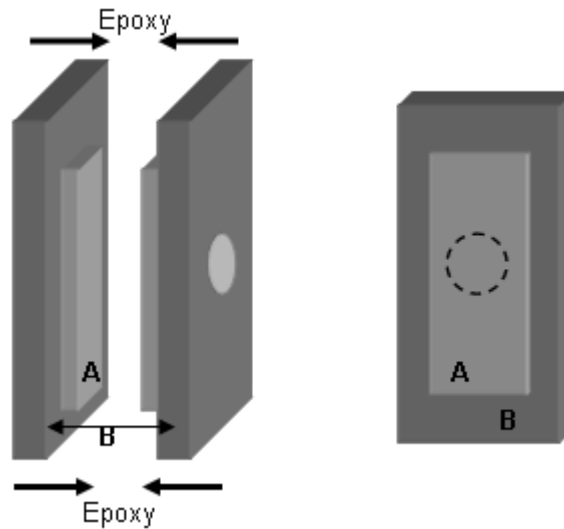


Figure 2.1. Schematic of a cell used in fluid measurements. Electrodes (A) are epoxied on G10 supports (B). Two electrode/G10 pieces are then epoxied together to form a complete cell. The dashed circle represents a hole drilled in the G10 so that external wires can be soldered to the back of the electrodes.

Electrodes, with typical dimensions of 7 x 19 mm, were cut out of metal sheets. The electrodes have been created with a variety of metals. Cu and Ni were commonly used; however, electrodes of Au, Ag, Pt, and stainless steel have also been made.

Support structures for the electrodes were made from G10 with dimensions of 7 x 27 mm. Holes were drilled in the center of the G10 pieces to accommodate external wires which were attached to the back of the electrodes later in the construction. The electrodes were then aligned on the G10 pieces, and the locations of the holes were marked on the back of the electrodes with a sharp blade. A bead of solder was placed at the marked location. The scoring with the blade facilitates the bonding of the solder to the electrode. Applying the bead of solder at this point is necessary simply because doing so after the electrode has been epoxied to the G10 risks overheating the epoxy and having the electrode separate from the G10. However, once the solder has bonded with the electrode, melting it to attach/remove wires presents little problem. In order to attach the electrodes to the G10, the surfaces of each were roughened and cleaned. Epoxy was applied to both surfaces and the pieces were placed on a work bench with the electrodes facing up. A paper towel soaked with isopropanol was placed between the pieces and a heavy weight. The pieces were allowed to cure overnight. Next, a spacer with the appropriate thickness was placed between two of the electrode/G10 pieces. The pieces were then clamped, and epoxy was applied to the ends of the G10 supports. After curing, external wires were attached.

Many cells designs were created and tested. The one described above performed the best. It has good insulating properties, and the capacitance of an empty cell is frequency independent over a broad frequency range.

2.4 ER Fluid Storage

The ER fluid samples were stored in glass vials with plastic, Teflon-lined caps. Silicone oil nearly perfectly wets many surfaces and has a tendency to leak from containers if not stored properly. Several steps, therefore, were taken to ensure that the fluid was stable over time. Two holes were drilled into the cap to accommodate the external, insulated, wires. Before fitting the wires through the holes, the insulation in the vicinity of the cap was removed, leaving a section of bare wire. There are two reasons for this. The epoxy, which is used to seal the holes in the cap, doesn't bond to the insulation well. It does, however, readily bond to metal. Secondly, even if a good bond is achieved between the epoxy and the insulation, silicone oil will escape between the metal wire and the insulation. With the insulation section removed, the surface of the cap was roughened, and the wires were inserted into the holes. Epoxy was generously applied to the entire surface of the cap. After curing, the cell/cap was cleaned with isopropanol to remove any residue from the epoxy. A photograph of a completed cell/cap is displayed in Figure 2.2.

After the cell is attached to the cap, the vial was filled with the ER fluid. The fluid was injected into the gap between the electrodes as well. The cell was then placed into the vial and the cap tightly secured. A paraffin film was wrapped around the cap and vial as final precaution against leakage and contamination.

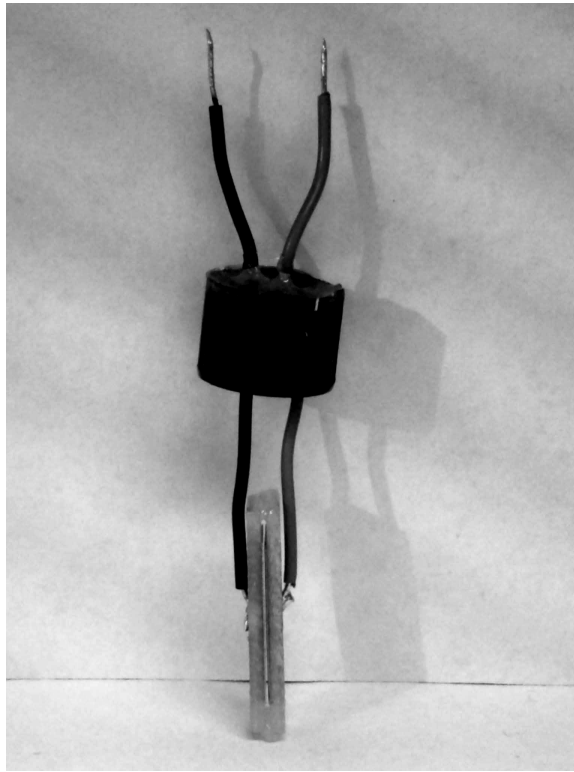


Figure 2.2. Photograph of a cap/cell.

2.5 Impedance Measurements

The word *impedance* describes the total opposition to current flow, due to resistive, capacitive, and inductive effects, in an *ac* circuit. When placed in such a circuit, materials themselves may display a combination of these effects which results in what is called the material's impedance. This is simply equal to the material's contribution to the total impedance of the circuit. The material is thought of as exhibiting such effects in parallel so that, in general, a material's impedance (Z) is described by

$$\frac{1}{Z} = \frac{1}{R} + i\omega C + i\frac{1}{\omega L}, \quad (2.1)$$

where $i = \sqrt{-1}$, ω is the angular frequency, R is the resistance, C is the capacitance, and L is the inductance of the material. As this project is a study of negative capacitance, inductive effects will not be considered. In fact, significant inductive effects were not found to be present in the ER fluid [3]. Thus, the ER fluid, in a measurement cell, can be thought of as possessing only a resistance and capacitance existing in parallel.

The current (I) flowing through such a configuration due to a voltage (V) is, from equation (2.1) without the inductive contribution,

$$I = V/Z = \frac{V}{R} + i\omega CV. \quad (2.2)$$

A phase difference exists between the current and the applied voltage. This is due to the presence of the imaginary component in (2.2). The phase angle (ϕ) is defined, by convention, to be equal to the negative angle between the current and voltage when plotted on the complex plane (see Figure 2.3). For simplicity, an angle $\theta \equiv -\phi$ was defined. In this case, a purely resistive element will have a phase angle of zero, and a material with a positive (negative) capacitance will yield a positive (negative) θ . Thus, one can conveniently determine the sign of the capacitance simply from knowledge of the sign of θ . In Figure 2.3, one can see that $\text{Re}(I)$ and V both lie on the real axis. It is clear that the phase angle is equivalent to the angle between the vector I and the $\text{Re}(I)$. Thus, the phase angle can be determined by

$$\tan(-\phi) = \omega RC. \quad (2.3)$$

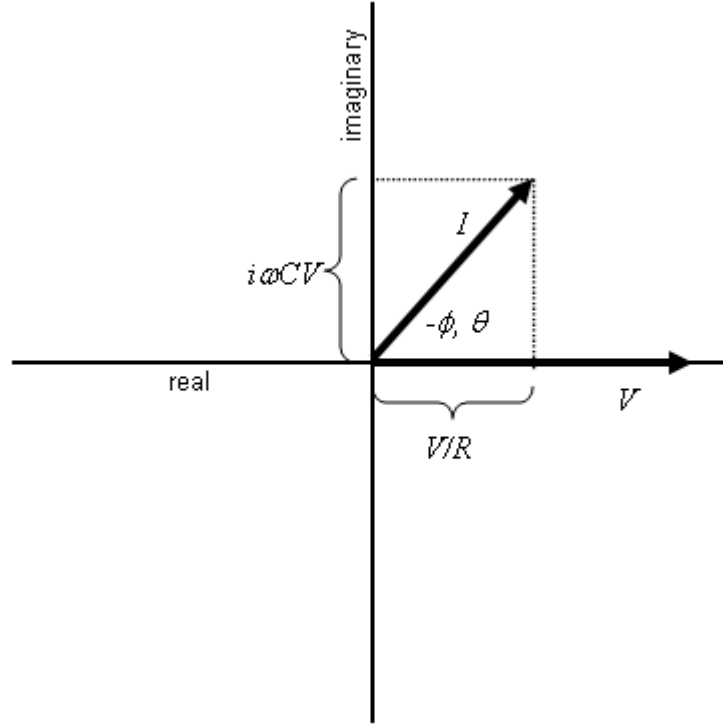


Figure 2.3. Phasor diagram of the current and voltage.

By measuring the current flowing through the material due to an applied voltage, one can determine the impedance, *i.e.*, the resistance and capacitance of the sample under study. These values depend not only the material properties, but also on the sample geometry. In other words, resistance and capacitance are extrinsic properties. Often, it is convenient to remove the geometric contributions so that one can examine the properties of the materials. Typically, in our experiments, the sample was an ER fluid in a cell with a cross sectional area of A and gap distance of L . The sample properties are described by the impedance or its inverse, the admittance, of the cell. From (2.2), the admittance can be written as

$$\tilde{Y} = \frac{1}{R} + i\omega C. \quad (2.4)$$

By removing the geometric factor of the cell, one can define the complex conductivity ($\tilde{\sigma} = \sigma' + i\sigma''$) of the material. The admittance is then $\tilde{Y} = \frac{A}{L} \tilde{\sigma}$ with $\sigma' = \left(\frac{L}{A}\right) \frac{1}{R}$ and $\sigma'' = \left(\frac{L}{A}\right) \omega C$.

Additionally, one can define a complex capacitance ($\tilde{C} = C' - iC''$) such that

$$\tilde{C} = \frac{-i}{\omega} \tilde{Y} = C - i \frac{1}{\omega R}. \quad (2.5)$$

The negative sign in the imaginary part of $\tilde{C}$ is a convention defined such that $C'' = \frac{1}{\omega R}$ is a positive quantity. Again, the geometric factors can be removed to obtain a material dependent quantity, the complex dielectric constant

$$\tilde{\epsilon} = \tilde{C} / C_o, \quad (2.6)$$

where $C_o = \frac{A}{L} \epsilon_o$ is the capacitance of the empty cell and ϵ_o is the permittivity of free space. These values will often be used in discussion and presentation of results.

Experimentally, in order to determine the complex impedance of a sample, an *ac* voltage is applied, and the current flowing through it is measured. As discussed in Chapter 1, the physical properties of the ER fluid are sensitive to *dc* electric fields. One might presume that the electrical properties of such a material would be field dependent as well. Therefore, most of our impedance experiments were performed in the presence of a *dc* bias voltage so that the total voltage applied was $V_{dc} + |V_{ac}| \sin(\omega t)$. The

impedance was probed using a broad range of frequencies from $10^{-5} - 10^5$ Hz. A typical circuit used to measure the impedance of our samples is shown in Figure 2.4.

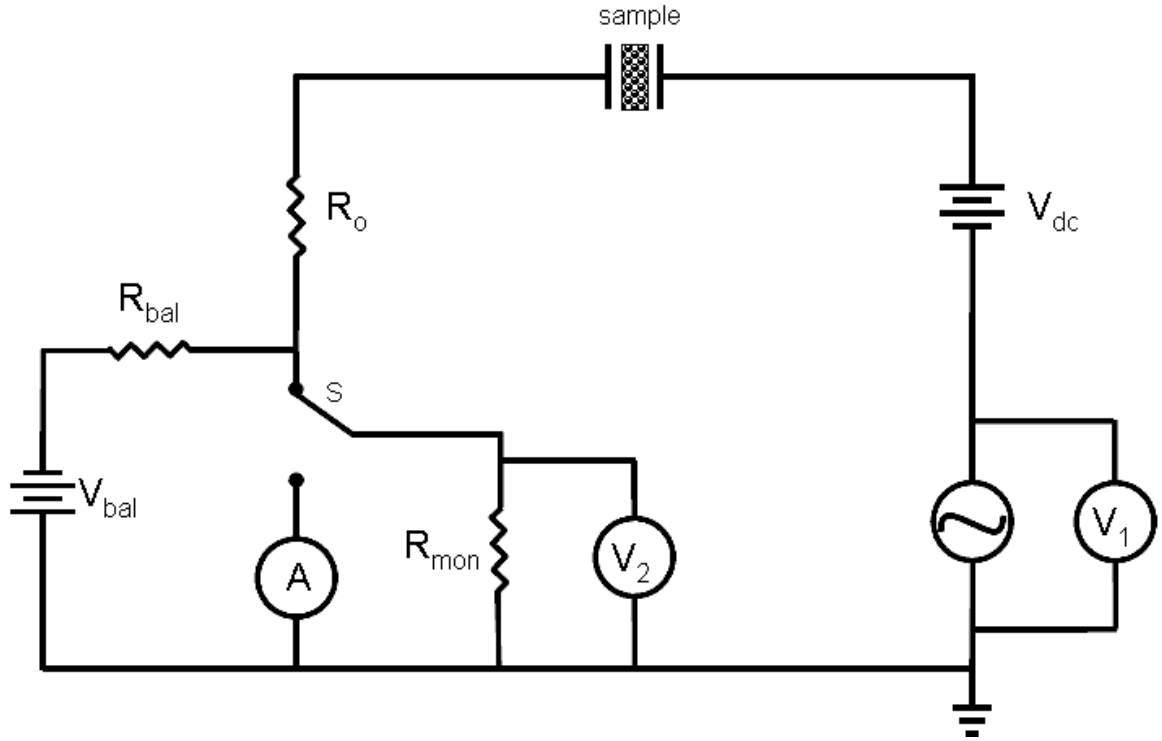


Figure 2.4. Circuit used in impedance measurements. Both *ac* and *dc* voltages are applied. The switch (S) determines if the current is measured by the voltage drop (V_2) across a resistor (R_{mon}) or directly by an ammeter. V_{bal} is a balancing voltage that removes the *dc* signal from the measured current.

The small *ac* excitation ($V_1 \approx 1$ V) was typically provided by a Stanford Research SR830 or SR850 lock-in amplifier. This was directly coupled to a *dc* power supply (Keithley 248 or Keithley 2400). Care must be taken to ensure that the low voltage terminal on the power supply is floating and not connected to the chassis ground (ground of the lab's power grid). An offset resistor (R_o) was placed in series with the sample to act as a current suppressor and protect the equipment in the event of a short in the

sample. The current flowing through the sample was either directly measured by the lock-in's built-in ammeter or, for low frequency measurements ($f < 1$ Hz), calculated from the voltage drop across a monitoring resistor (R_{mon}) of known value ($I = V/R_{\text{mon}}$). The later case utilized an HP 34420A nanovoltmeter to measure the voltage drop (V_2) across R_{mon} . Another nanovoltmeter was then used to record the applied *ac* voltage (V_1). This type of measurement was useful when raw current vs. time data was required or if the lock-in was not used to provide the *ac* excitation. The values of R_o and R_{mon} were chosen such that $R_o + R_{\text{mon}} \ll R_{\text{sample}}$, guaranteeing that the voltage drop across the sample was as close to V_{dc} as possible. Typical values of R_o and R_{mon} were 1 M Ω and 100 k Ω , respectively. In order to improve the accuracy of the measurement, a second *dc* power supply (V_{bal}) as added to subtract the *dc* signal out of the measured current. At times this was necessary as the *dc* current would overload the ammeter. Additionally, when using the nanovoltmeters, the balancing voltage would allow the measurement range of the nanovoltmeter to be minimized, thus increasing the number of relevant digits recorded and maximizing the accuracy. For example, the nanovoltmeter records 7 digits of voltage. If the *dc* voltage drop across R_{mon} is 20 V, the voltmeter will read the 20 V plus 5 digits of *ac* voltage. Thus, the *ac* voltage will be known to the 10 μ V level. However, if V_{bal} is tuned to remove the 20 V signal, then the meter is free to use all 7 digits on the *ac* signal.

After recording the raw data, the effects of the various components in the circuit, *e.g.*, R_o , R_{mon} , output impedances of the lock-in and the *dc* power supply, were

subtracted in order to isolate the effect of the sample on the current. Once this is known, the sample's impedance can be calculated from equation (2.2).

Measurements were sometimes performed at very low frequencies, $f < 10^{-3}$ Hz, which is below the lock-in's frequency range. In this case, a Keithley 2400 was used to generate the *ac* signal. The 2400 is a *dc* power supply, but it can, when controlled by a computer, simulate a sinusoidal excitation if the frequency is sufficiently small. Since the lock-in cannot be used at these low frequencies, the current was measured by the voltage drop across R_{mon} as described above.

Achieving an accurate measurement was of primary importance. To this end, the circuit was tested with many resistor/capacitor combinations over the entire frequency and voltage ranges used in the experiments. Of particular interest was the phase angle resolution of the circuit. Ideally, a resistor will yield a current exactly in phase with the voltage, *i.e.*, a phase angle equal to zero. Any deviation from zero will be the phase angle resolution of the circuit. This resolution was tested using resistors with values equal to that of the ER fluid at different biases over the entire voltage and frequency ranges. The uncertainty of the phase angle ranges from 0.01-0.05°. This is much smaller than the phase angles created by the impedance of the ER fluid, which are generally larger than 0.5°. Figure 2.5 displays the results of the phase resolution investigation. The width of the gray line indicates the uncertainty in the phase. The data points represent the phase angle of the ER fluid at various biases. It is clear that the circuit has sufficient resolution to determine the impedance of the ER fluid.

The accuracy of the experiment was further tested by using different components in the circuit. For example, the results of the high frequency experiments, which were

performed with the lock-in amplifier, were confirmed when a Keithley 3330 LCZ meter was used as the source/measurement device. Figure 2.6 shows the capacitance of the ER fluid obtained using different measurement devices. There is good agreement between the experiments performed with the different measurement devices as evidenced by the data overlap at the common frequencies.

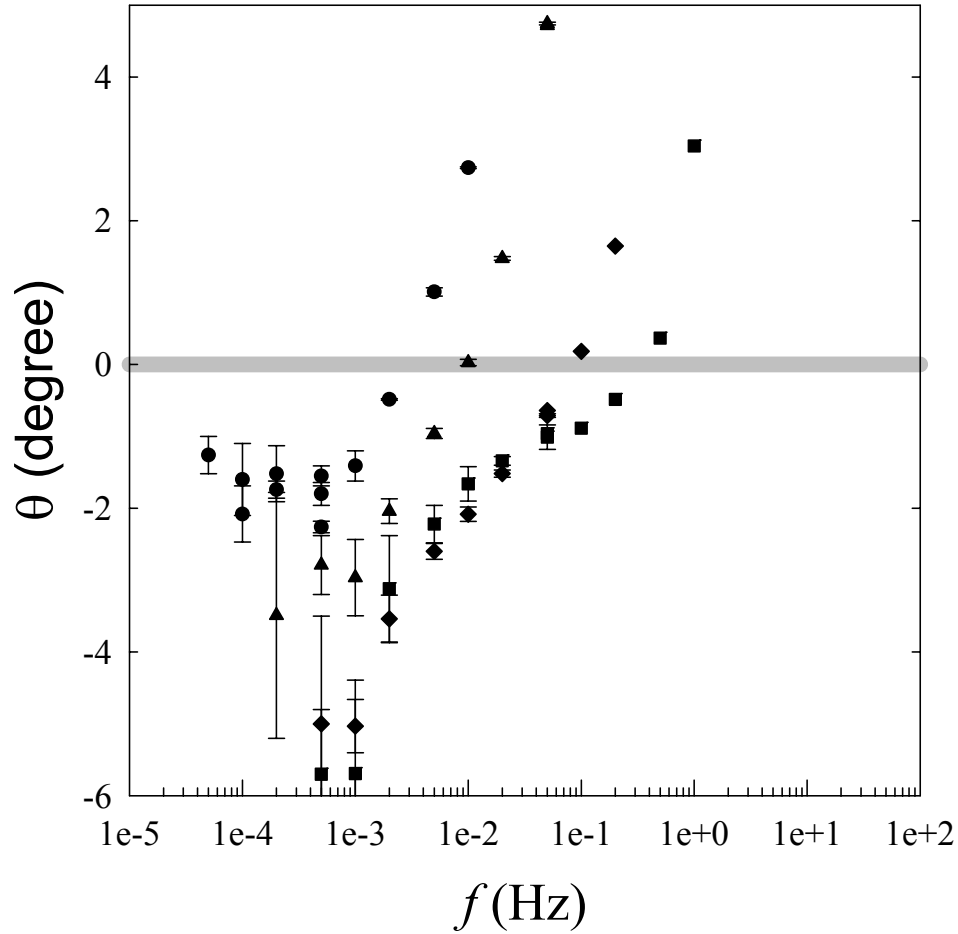


Figure 2.5. Phase angles of the ER fluid for biases of 50 V (●), 100 V (▲), 200 V (◆), and 350 V (■). The width of the gray line represents the phase resolution. The resolution is significantly smaller than the angles measured indicating the experiment is sufficiently sensitive to changes in phase.

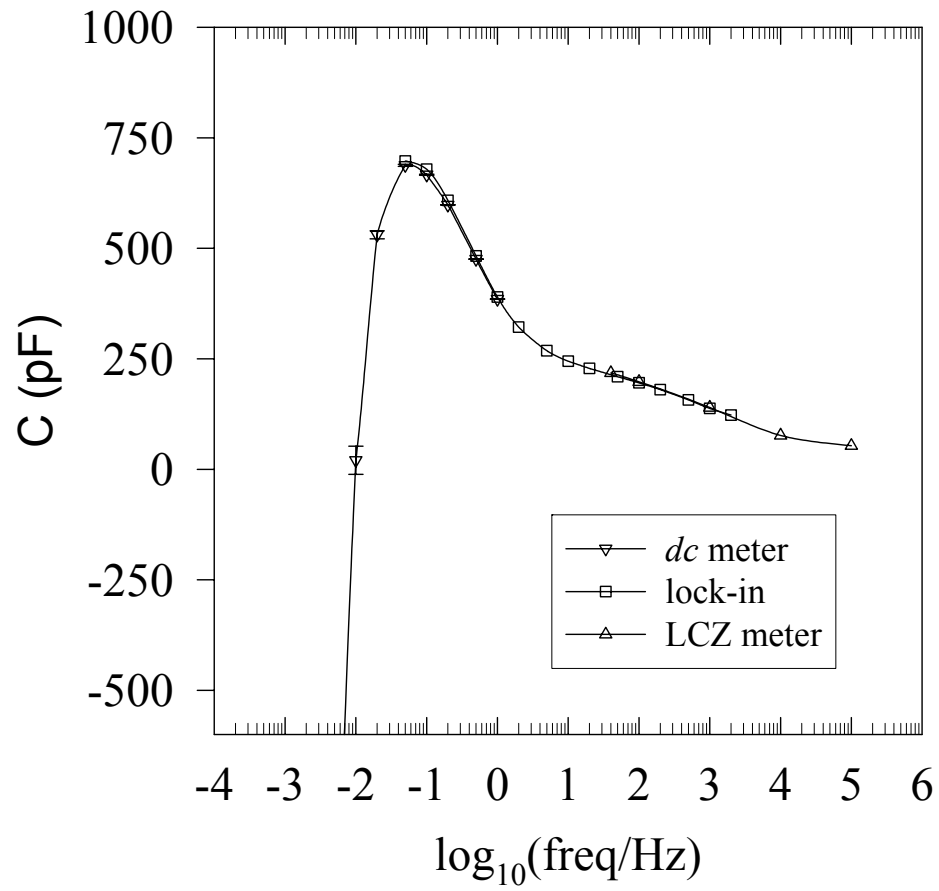


Figure 2.6. Capacitance of the ER fluid under an electric field of 1 kV/mm. The data were taken with three measurement devices corresponding to different regions in frequency. The measurements agree in the overlapping frequency regions indicating that the results are valid.

2.6 I-V Loop Measurement

The I-V loop measurement is a variation of the impedance measurement described in the previous section. In fact, the two measurements share a common circuit (Figure 2.4). The central difference lies in how the data is plotted and analyzed. This method uses the *dc* meters to record the *ac* excitation and voltage drop across R_{mon} and, thus, is practical only for frequencies below 1 Hz. This technique is useful when it is necessary to concurrently measure the *dc* and *ac* current. Additionally, one can easily subtract out extraneous effects, such as those associated with conductance drifts that plague low frequency experiments of the ER fluid.

The capacitance is a measure of how much charge (Q) can be stored on a conductor at a particular voltage (V). Mathematically, the capacitance is the proportionality constant between the two values:

$$Q = CV. \quad (2.7)$$

Current is defined as the change of charge with time:

$$I = \frac{dQ}{dt}. \quad (2.8)$$

One can see from equations (2.7) and (2.8) that the current due to a time dependent voltage acting on a capacitor of constant value is simply

$$I = \frac{dQ}{dt} = \frac{d(CV)}{dt} = C \frac{dV}{dt}. \quad (2.9)$$

Incidentally, one can use equation (2.9) to derive the impedance of a capacitor by Fourier transforming both sides from the time domain to the frequency domain (the derivative provides a factor of $i\omega$).

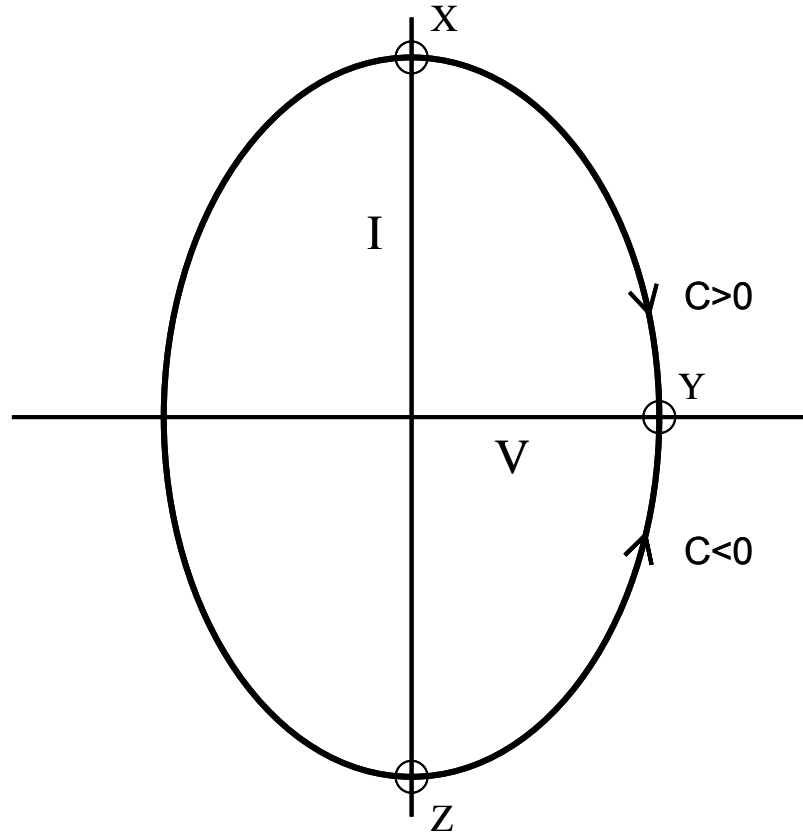


Figure 2.7. Current vs. voltage plot for an ideal capacitor subject to a sinusoidal excitation. The loop is traced in a clockwise direction for a positive capacitance. It is traced in a counterclockwise direction if the capacitance is negative.

Consider an impedance measurement of an ideal capacitor, that is, a lossless capacitor of value C which is independent of both frequency and voltage. The current, due to an excitation $|V_{ac}|\sin(\omega t)$, can be calculated from (2.9):

$$I = C\omega|V_{ac}|\cos(\omega t). \quad (2.10)$$

Figure 2.7 shows a plot of the current vs. voltage. Initially, at $t = 0$, the voltage is zero, and the current is at its maximum value. This corresponds to point X. One quarter of a

cycle later ($t = \frac{\pi}{2\omega}$), the voltage has obtained its maximum value while the current is zero (point Y). This continues in time. In this manner, an oval is traced as the voltage oscillates. Each cycle of the voltage will trace one oval in the clockwise direction.

The situation is different, however, if C is negative. In this case, the current is initially at its most negative value when the voltage is zero (point Z). One quarter of a cycle later, the trace has reached point Y. Thus, in the case of a negative capacitance, the oval is traced in the counterclockwise direction. It is clear that one can quickly determine the sign of a capacitance by observing an I-V loop traced in time.

The magnitude of the capacitance can be calculated by first noting that the maximum current occurs on the y-axis, when $\cos(\omega t) = 1$. So

$$C = \frac{I_{\max}}{\omega |V_{ac}|}. \quad (2.11)$$

The arguments described above apply equally well to a parallel RC network or a lossy capacitor. In this case, however, the loop appears rotated due to the presence of the resistor, which adds a second term to the ac current. This resistive term is in phase with the excitation, and thus does not yield a loop, but a line in the case of a linear resistance or a curve if the resistance is nonlinear. The total current in such a configuration was given in equation (2.2). If, for example, one measures a material with a resistance $R = 5 \text{ M}\Omega$ and capacitance $C = 100 \text{ pF}$ with an ac voltage of magnitude equal to one and frequency $f = 100 \text{ Hz}$ such that $V = \sin(2\pi * 100 * t)$, the resulting I-V graph will appear as displayed in Figure 2.8a. The capacitance is positive, so the trace runs in a clockwise direction. The resistive contribution can be isolated by taking the

average of the current in the voltage increasing and voltage decreasing branches of the loop. This average is the current flowing through the resistive channel of the RC network and is represented as the dotted line in Figure 2.8a. From (2.2), this current is $I_R = \frac{V}{R}$. Thus, the resistance can be determined by taking the inverse of the slope of the line representing I_R . The capacitive contribution can now be calculated by subtracting I_R from the total current. This subtraction results in a plot of the “ideal capacitor” type described above and is shown in Figure 2.8b. The capacitance is given by (2.11).

If a dc bias is present, the measured voltage and current are offset by the dc contribution to the respective values. Graphically, this results in a loop that is translated by V_{dc} and I_{dc} . One can easily determine the dc current by taking the average, or finding the midpoint, of the line representing the resistive contribution. If a balancing voltage was applied, as described in the previous section, then this contribution must be added to the line average.

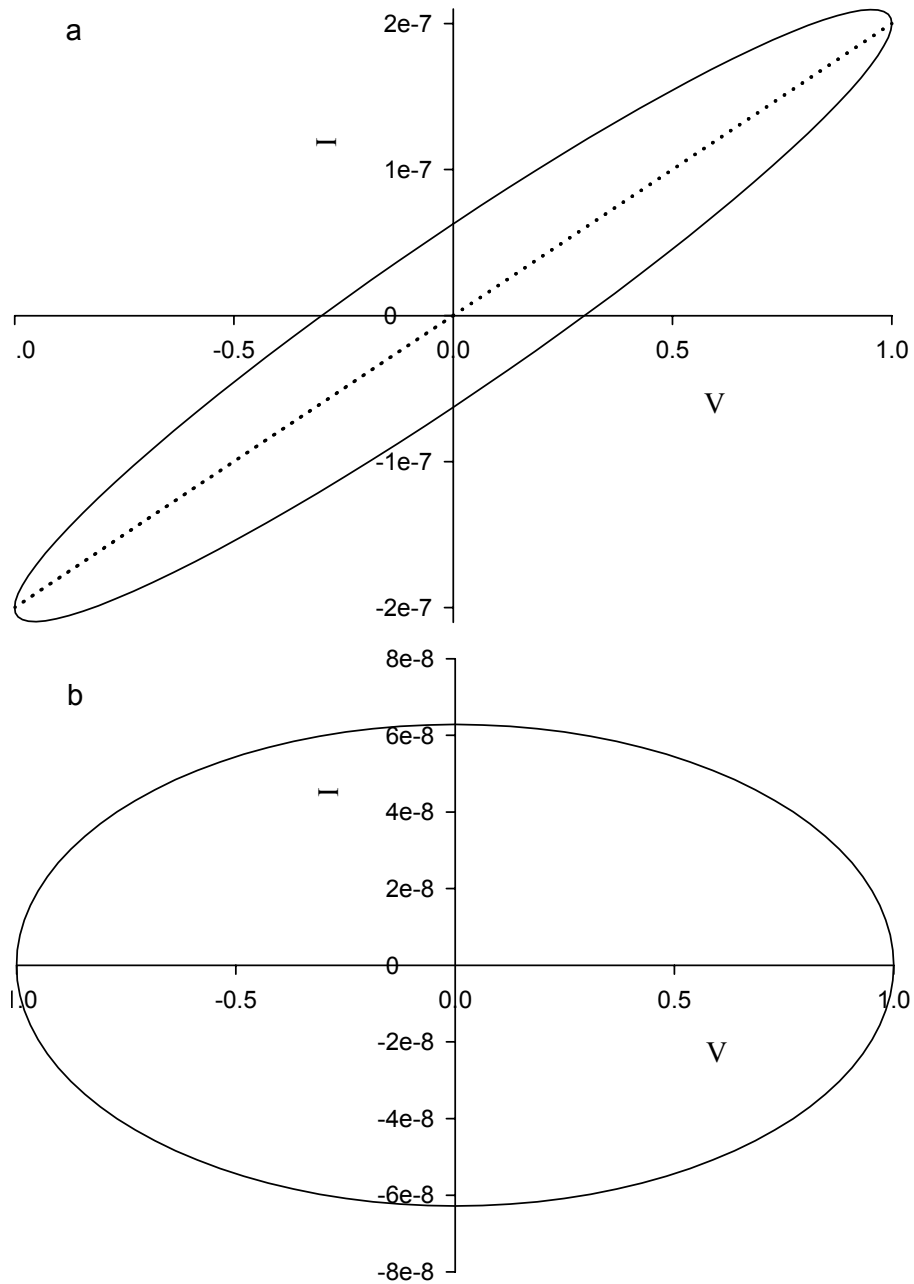


Figure 2.8. a) The I-V loop (calculated) for an RC network with parameters described in the text. The dotted line represents the contribution from the resistive component, with the slope = $1/R$. b) The capacitive contribution to the I-V loop. This is calculated by subtracting the resistive contribution from the total I-V in (a).

2.7 Transient Current Measurement

The measurements described in the previous sections are examples of frequency domain experiments. In addition to measurements of this type, time domain experiments have also been performed. Mutually supportive data from these two types of experiments are valuable because it bolsters confidence in the validity of the results.

The circuit used in the time domain experiments is shown in Figure 2.9. In this case, the only voltage applied is from a *dc* power supply. The power supply applies step function excitations to the sample. The time dependence of the resulting current is measured by the voltage drop across R_{mon} . Again, the role of R_o is to suppress the current in the event of a short.

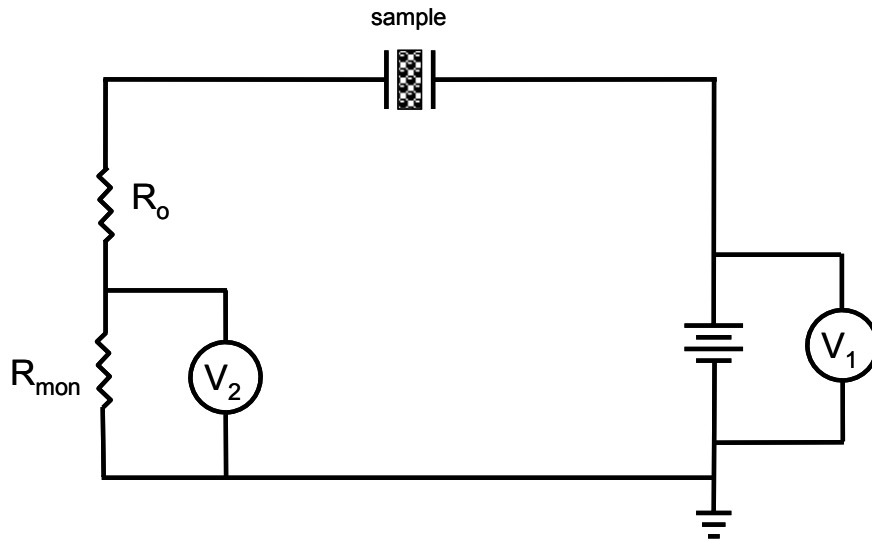


Figure 2.9. Circuit used in transient current experiments.

In most experiments a *dc* bias is required. The computer controlled power supply was simply programmed to source $V_{dc} + \Delta V$. In order to accurately resolve the

dc baseline, a series of step function excitations of alternating signs was applied to the sample. The current will decay to the baseline from above and below. The common asymptote was defined as the *dc* baseline. The transient current can be calculated by subtracting the *dc* baseline from the total current.

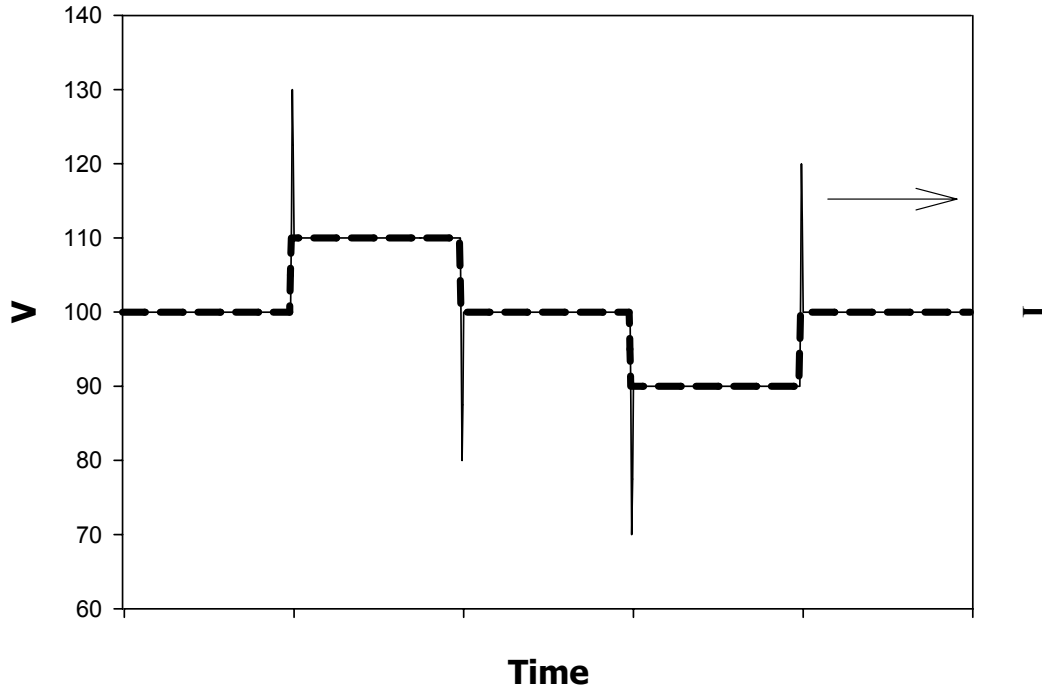


Figure 2.10. Predicted results from a transient current experiment performed on a parallel RC configuration. The voltage is shown as the thick dashed line. The current is represented by the solid line. The spikes in the current are due to a surge in the current in the capacitive channel immediately after a change in voltage.

Figure 2.10 shows the predicted results of the time domain experiment performed on a parallel RC network with constant values. The $V(t)$ graph is displayed as the thick dashed line in the figure. Here, a *dc* bias of 100 V is present, and the step functions have an amplitude of 10 V. The current, for the most part, mimics the shape of the voltage graph. However, there is a sharp jump in the current immediately after the voltage

changes. Initially, the capacitor acts as a short and the current is large. As charge starts to build up, the current slows. Soon, the plates are saturated with charge and the current can only flow in the resistive channel, yielding a constant current of V/R .

2.8 Chapter References

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Chapter 3: Results and Discussion

This chapter presents and discusses the experimental results obtained during the course of the project. It will begin with the results from impedance experiments on the ER fluid. This is the cornerstone of our work as it not only highlights the unusual characteristics of the capacitance but ultimately provides the explanation for such properties. The frequency domain examination will then be compared to the results of our time domain experiments. Next, the relationship between negative capacitance and dielectric constant will be discussed. This will be followed by some general dielectric properties of the ER fluid. The chapter will conclude with a discussion of the relationship between the conductivity and the negative capacitance of the fluid.

3.1 Impedance of the ER Fluid: $1/R$ and C

Typical dielectric behavior of condensed matter systems was reviewed in Chapter 1. In particular, it was stated that true Debye dispersions are almost never observed. In their place, one commonly finds the universal dielectric response (UDR) of disordered solids which is characterized by a fractional power law dependence of the real and imaginary parts of the susceptibility vs. frequency [1, 2, 3].

Impedance measurements of the type described in Section 2.5 were performed on the ER fluid. $\frac{1}{R(\omega)}$ and $C(\omega)$ are shown in Figure 3.1a, b, respectively. With $V_{dc} = 0$,

the capacitance and conductance possess a rough UDR dispersion. The capacitance exhibits significant low frequency dispersion by increasing several orders of magnitude as the frequency is lowered. In the conductance, slight deviations from the typical UDR dispersion are observed. However, for the most part, in the absence of a *dc* bias, the ER fluid behaves as a typical disordered material.

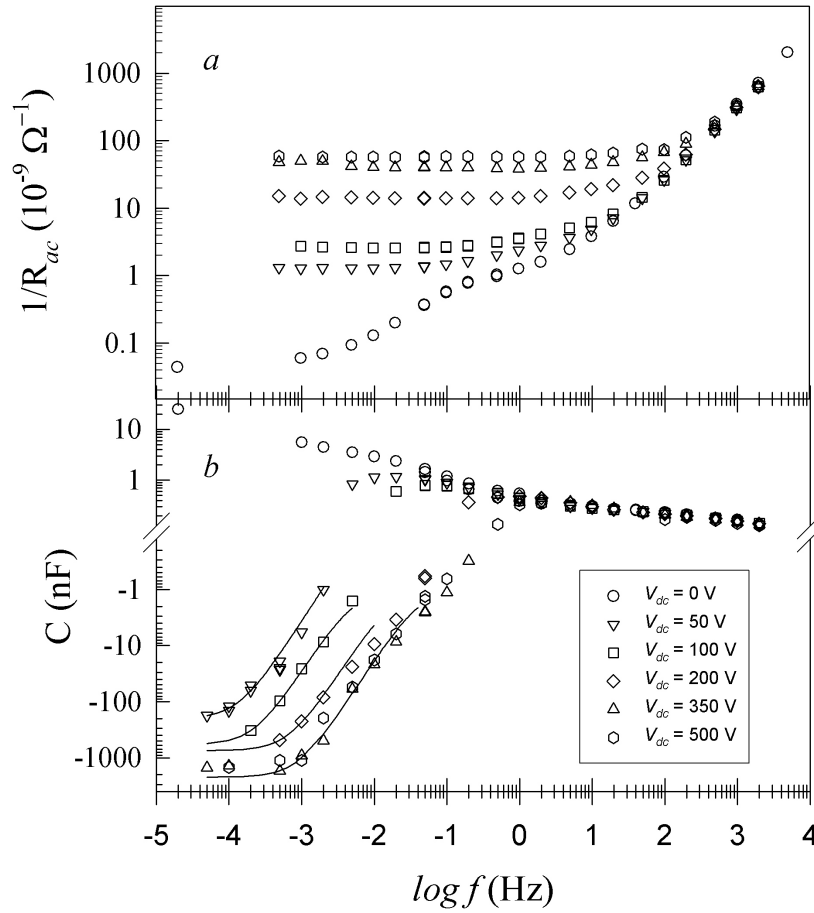


Figure 3.1. The conductance (a) and capacitance (b) of the ER fluid at various *dc* biases. UDR behavior and linearity are present at high frequencies. At low frequencies the capacitance has a plasma-like dispersion (solid lines in b).

With the application of a dc bias, the UDR behavior is maintained at high frequencies. Additionally, the conductance is field independent in this region, indicating that the material is linear at high frequencies. The situation, however, is different at low frequencies. The conductance becomes V_{dc} dependent, *i.e.*, nonlinear, and nearly frequency independent. More interestingly, the capacitance deviates from the UDR dispersion and becomes strongly negative, changing several orders of magnitude in a few decades of frequency. The magnitude of the negative capacitance (NC) and the frequency at which the transition to negative values occurs is bias dependent, except at the largest biases where the NC is independent of voltage.

Recall, from Chapter 1, that the susceptibility of a damped plasma, with particles of charge $-e$ and mass m , is negative and of the form

$$\chi'(\omega) = \frac{-\omega_p^2}{\omega^2 + \gamma^2}, \quad (3.1)$$

where

$$\omega_p = \sqrt{\frac{e^2 N}{\epsilon_o m}} \quad (3.2)$$

is the plasma frequency, γ is the damping parameter, and N is the number of particles per unit volume. Equation (3.1) describes the frequency dependence of the low frequency capacitance rather well, as evidenced by the solid fits to the data in Figure 3.1b. This, however, should be interpreted with caution. A plasma-like dispersion of the form of (3.1) and shown in Figure 3.1b does not necessarily require free charge carriers to be responsible for the low frequency capacitance in the ER fluid. This is highlighted by a simple calculation involving the plasma frequency. With $V_{dc} = 50$ V, $\omega_p^2 \approx 0.19$.

Assume that the charge carriers are electrons. By solving (3.2) for N and substituting the appropriate values, one obtains $N = 6 \cdot 10^{-5}$ charges/m³. With a cell volume of approximately $8 \cdot 10^{-9}$ m³, the total number of charges in the measurement cell is the unphysical value of $5 \cdot 10^{-13}$. Clearly, a free plasma, as described in Chapter 1 cannot be responsible for the negative capacitance. One can take the analysis a step further by asking if charged nanoparticle motion is responsible for the plasma-like behavior. The large mass of the nanoparticles will increase the number density by many orders of magnitude. If one assumes the nanoparticles are minimally charged (with charge e), the number density will be maximized. The mass of the nanoparticles can be approximated by using the density of BaTiO ($\rho = 4.5 \cdot 10^3$ kg/m³). One can calculate the volume of a nanoparticle by assuming a spherical shape and radius of 80 nm. This results in a volume of $2 \cdot 10^{-21}$ m³. Then, the mass is approximately 10^{-17} kg. Substituting this value into (3.2) and solving for N yields, $N = 6 \cdot 10^8$ particles/m³. The number of particles in the cell with charge e is $NV_{cell} = 5$. So, out of all the nanoparticles in the cell, five of them would have a charge and contribute to the plasma-like dispersion. This is, of course, an unphysical result as well. Thus, it is clear that the negative capacitance observed in the ER fluid is not due to inertial effects on charged particle or nanoparticle motion, as is the case in a plasma.

Whatever the cause, it is clear that the NC does possess a plasma-like dispersion. A low frequency capacitance of this form implies that the static ($\omega = 0$) capacitance is negative. If the capacitance is associated with a dielectric constant, then the static dielectric constant will be negative as well. This is noteworthy because the existence of

a negative static dielectric constant is highly controversial [4]. Additionally, a material with such a property has never been reported.

As long as the complex admittance is analytic^{*}, the presence of this plasma-like capacitance should be reflected in $\frac{1}{R(\omega)}$ as the in-phase counterpart to equation (3.1).

In Chapter 1, this component was derived and displayed in Figure 1.2. It was shown that the conductivity

$$\sigma'(\omega) = \epsilon_o \frac{\omega_p^2 \gamma}{(\omega^2 + \gamma^2)}. \quad (3.3)$$

Strangely, the conductance in Figure 3.1 has what appears to be a UDR-like dispersion, as indicated by the frequency independence and power law behavior at low and high frequencies, respectively [3]. However, a closer examination reveals that, at $V_{dc} \neq 0$,

$\frac{1}{R(\omega)}$ does vary non-monotonically with ω . This can be seen (Figure 3.2) by

subtracting an ω independent baseline from $\frac{1}{R(\omega)}$ in Figure 3.1a. This results in a “dip”

that occurs at approximately the same frequency as the onset of the NC for each bias voltage.

The existence of a dip seems reasonable. The plasma-like conductivity in equation (3.3) decreases with the increase of frequency. The high frequency UDR dispersion increases. Therefore, the combination of the low frequency plasma dispersion and the high frequency UDR would naturally lead to a dip in the conductance at the

^{*} From Figure 3.1, the ER fluid is clearly nonlinear. Any arguments involving analyticity would normally be invalid. However, in the small signal limit, the relationship between I_{ac} and V_{ac} is a linear one. R and C of the ER fluid are measured in this limit, and thus, the analyticity of the admittance is maintained.

onset of NC. Thus, it appears that there are two competing dielectric relaxations in the ER fluid, the UDR, which dominates the conductance and the high frequency capacitance, and the plasma-like behavior that dominates the capacitance at low frequencies. A similar competition between, non-plasma-like, NC and UDR has been proposed in doped silica glasses, with the UDR managing to suppress the NC in that case [5]. A more through examination, presented later in the chapter, will confirm the existence of this plasma-like component in the conductance of the ER fluid.

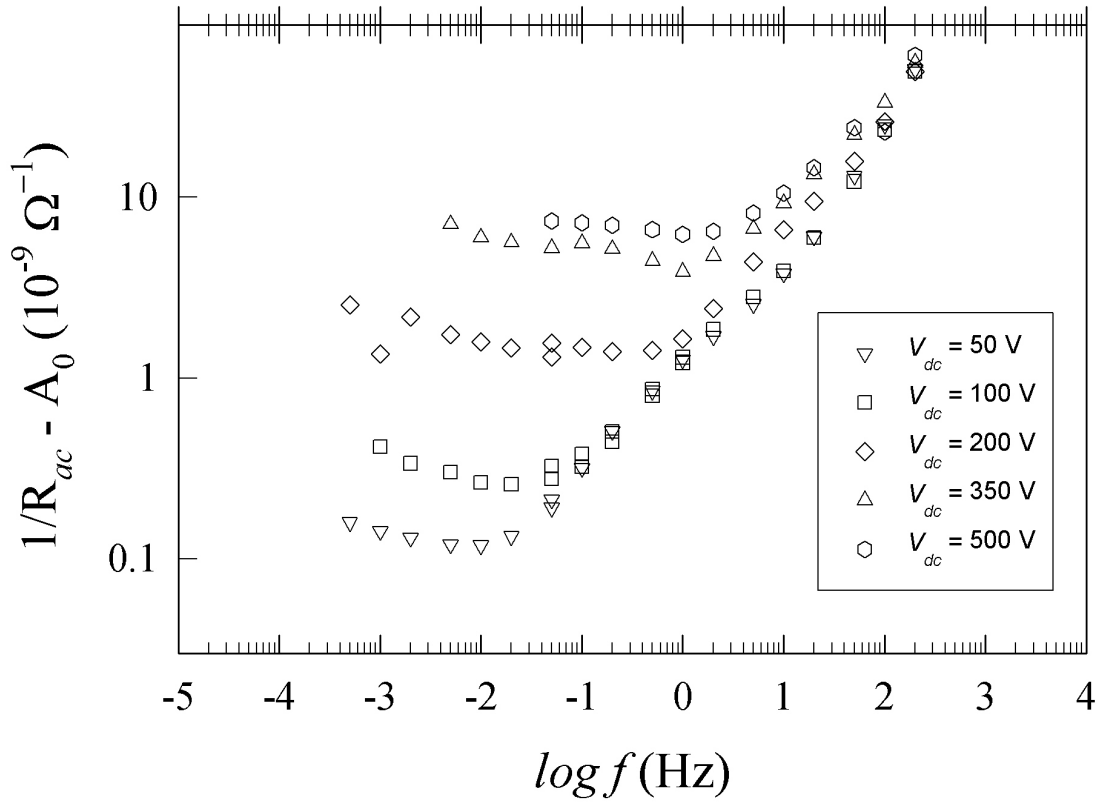


Figure 3.2. The conductance minima. $A_0 = 0.9 / R_{\max}(V_{dc})$ is a baseline subtracted for clarity. The minimum is due to a plasma-like dispersion at low frequencies combined with a UDR dispersion at high frequencies. The nonlinearity is enhanced below the minimum.

It should be noted that, in Figure 3.2, one can see an increase of the V_{dc} splitting in the conductance below the dip. This indicates an enhancement of the material's nonlinearity at frequencies where the capacitance is negative. This important effect will be discussed later in the chapter as well.

3.2 Transient Response

The previous section dealt with the frequency response of the ER fluid. It should be instructive to examine this response in the time domain as well. At the very least, mutually supportive data in the time and frequency domains will confirm the accuracy and validity of the two types of experiments. On the other hand, disagreement between these results indicates a problem with at least one of the experiments. Time domain experiments will also provide insight into the material's relaxation after an excitation. Furthermore, it has been suggested that a time domain experiment is a more intuitive method of examining NC than a frequency domain investigation, which is how capacitance is normally studied [1, 6].

The details of the time domain experiments were provided in Section 2.7. To summarize, a dc source is used to provide a series of step function excitations superimposed on a bias voltage. The current flowing through the sample is measured as a function of time. The response of a constant resistor and capacitor in parallel to this type of voltage excitation was shown in Figure 2.10. In that case, the characteristic feature was a large spike in the current immediately after the voltage changed followed

by an exponential decay to the *dc* level with a time constant equal to the product RC . The transient response can be determined by subtracting the *dc* baseline from the total measured response.

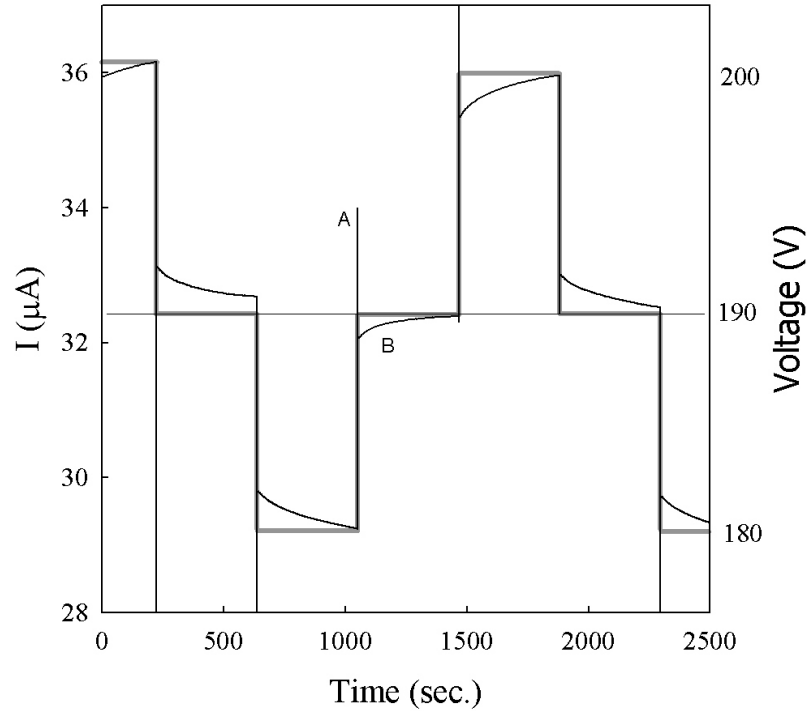


Figure 3.3. Current vs. time due to 10 V step excitations superimposed on a 190 V *dc* bias. The voltage is represented by the thick gray line. After an increase in voltage, the current spikes (A) and then falls below the baseline before its final decay (B). A similar, but opposite, effect is seen after a decrease in voltage.

The ER fluid was measured in this manner with a series of ± 10 V step excitations on a constant 190 V *dc* bias. Figure 3.3 shows the measured current flowing through the fluid vs. time. A schematic of the applied voltage is included for reference. The behavior is significantly different from the constant RC case. Upon a positive 10 V

voltage step, *e.g.*, from 180 to 190 V, the current spikes as it does for the RC network (point A in Figure 3.3). However, instead of directly decaying to the baseline, the current very quickly crosses the baseline and then begins its decay (point B). This is a dramatic deviation from typical behavior. The scale of Figure 3.3 masks the details of the decay. The effect can be seen more clearly, however, by subtracting the baseline to obtain the transient current due to the excitation. This is displayed as the data points in Figure 3.4.

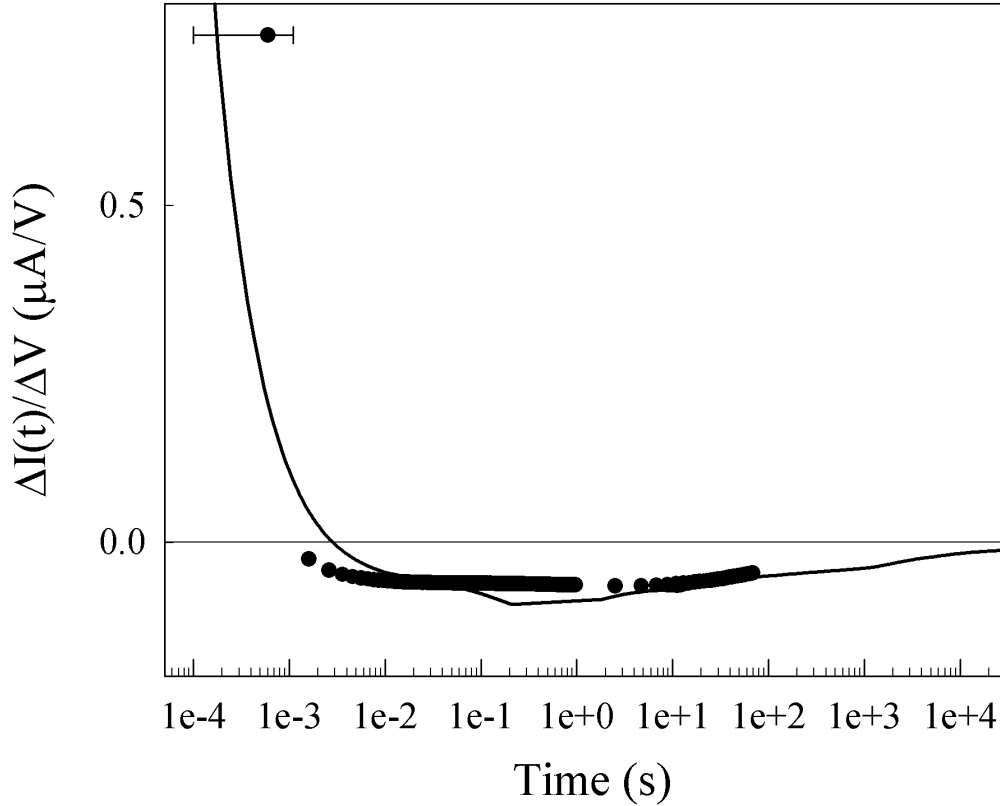


Figure 3.4. Scaled transient current due to a 10 V step excitation with a bias of 190 V. Data points are from measured time domain data. Solid line is from calculation based on frequency domain data. Both predict a current that is initially positive but becomes negative after 1 ms. The current decays over many decades in time.

The early current spike is positive. This is due to the positive, high frequency capacitance of the cell. The measurement error of this spike, indicated by the error bars, is rather large due to the triggering time of the voltmeter. Since the current drops so rapidly, any change in the time of the initial measurement reading will result in a significant change in the measured current. Nevertheless, the spike is clearly positive. However, after 1 ms, the current decreases to zero and continues to negative values. It then decays back to zero over several orders in magnitude in time. This is a remarkable effect. A transient current with negative values is flowing against the electric field. This current flows against the electric field for an extended period of time.

This curious effect has been verified by a calculation based on frequency domain data. Figure 3.1 shows the conductance $\frac{1}{R(\omega)}$ and capacitance $C(\omega)$ of the fluid over a range of frequencies with a *dc* bias of 200 V. With these, one can calculate the current in the frequency domain due to a step function excitation:

$$I(\omega) = \left[\frac{1}{R(\omega)} + i\omega C(\omega) \right] V(\omega). \quad (3.4)$$

Here, $V(\omega)$ is the Fourier transform of a step function voltage in time. This current can be transformed into the time domain with an inverse Fourier transform. The result is shown as the solid line in Figure 3.4. It is clear that there is good agreement between the time domain data and the calculation based on the frequency domain data. This is the mutual support mentioned earlier. The agreement indicates that both experiments have been performed correctly and the results are valid.

A note of caution should be mentioned here. Fourier transforms are only valid for linear systems. A glance at Figure 3.1 shows that the admittance of the ER fluid is bias dependent at 200 V. As mentioned above, $R(\omega)$ and $C(\omega)$ have been measured in the small signal limit where there is a linear relationship between the current and the voltage. The issue lies in the 10 V voltage excitation, which is outside the small signal limit. This nonlinearity calls the agreement of the time and frequency domain data into question. Fortunately, Fourier transforms have been known to show some level of tolerance to the presence of nonlinearities in materials [7], even if they are not valid in the strict mathematical sense. This certainly appears true for the present case, where the exceptional agreement is strongly convincing. This is supported by similar results obtained in the high bias regime, where there is a weaker voltage dependence [8].

3.3 Relationship Between NC and the Dielectric Constant

As indicated above, an important aspect of NC in the ER fluid is the plasma-like dispersion. If the NC is associated with a dielectric constant, then the low frequency dielectric constant will be negative, possibly to the static limit. The relationship between various instances of NC and the dielectric constant of the material is rarely mentioned in the literature. In fact, almost all previous publications carefully use the term “negative capacitance” and avoid connecting it with a dielectric constant. This is understandable when referring to devices in which the NC originates at an

interface within the device or at an electrode. However, when NC is due to bulk processes, the use of a dielectric constant becomes appropriate.

Naively, one might think that a dielectric constant can be calculated by simply factoring out the geometric capacitance of the cell, *i.e.*,

$$\varepsilon = C / C_o . \quad (3.5)$$

While this is true in many cases, the situation is more complicated for nonlinear and leaky materials. The ER fluid is clearly nonlinear. However, R and C are measured in the small signal limit and thus, are immune to nonlinear effects. With the presence of a dc bias, the ε would be defined in the differential sense. Also, in a material with a nonzero conductivity, questions about the validity of (3.5) can be raised. A similar problem, fortunately, has been addressed for a classical free-carrier plasma [9]. It is claimed in Ref. 9 that the ε_1 defined in the admittance, $\nabla \cdot \mathbf{j} = (\sigma + i\omega\varepsilon_1)\nabla \cdot \mathbf{E}$, of a conducting medium should be exactly the same as the permittivity ε_p in the Maxwell equation $(\sigma + i\omega\varepsilon_p)\nabla \cdot \mathbf{E} = i\omega\rho_{\text{ext}}$ in the ω -domain. The authors of Ref. 9 further demonstrated that this equality should hold regardless the possible dispersions and medium anisotropy as long as the Fourier transformation is permitted. Strict linearity and Fourier transformation, however, are usually not a problem in the differential sense even if the overall I-V characteristic is nonlinear.

In order to determine whether the NC in a particular case represents a negative dielectric constant, therefore, one merely needs to exclude interface phenomena. If the NC in the ER fluid is due to an interface effect, a likely source would be at an electrode. NC measurements of the ER fluid have been made using electrodes of various metals

such as Cu, Au, Ni, Pt as well as indium-tin oxide (ITO). Such a wide array of materials makes an electrode effect an unlikely candidate as the source of the NC.

The most plausible scenario is an interfacial layer at an electrode with a conductance G_i in parallel with a plasma-like capacitance C_i . This interfacial layer would be coupled in series to the bulk of the fluid, represented by a parallel combination of G_b and C_b , which have a UDR frequency dependence due to the disordered nature of the fluid. However, for simplicity, it will be assumed that the capacitance channel will be dominated by the interface capacitance, and the bulk capacitance will be ignored for the moment. This situation is represented schematically in Figure 3.5. In this case, the impedance of the system would be

$$Z = \frac{1}{G_i + i\omega C_i} + \frac{1}{G_b}. \quad (3.6)$$

Here, $G_i \gg G_b$ due to the large dc resistance of the bulk. In the low frequency limit, the effective capacitance of the system, *i.e.*, the capacitance measured by an experiment, will be

$$C_{eff} = C_i \left(\frac{G_b}{G_i} \right)^2 = C_i \left(\frac{R_i}{R_b} \right)^2. \quad (3.7)$$

At 500 V, the experiments have determined that $C_{eff} = 10^{-6}$ F and $R_b = 10^7 \Omega$. An exaggerated value for the interfacial resistance, $R_i \approx 10^3 \Omega$, can be substituted in (3.7). This results in an interfacial capacitance of $|C_i| = 10^2$ F. Such an unusually large value casts doubt on the validity of this scenario. As the value of R_i decreases, the $|C_i|$ required to generate the measured capacitance increases further. Additionally, the inclusion of the positive bulk capacitance worsens the situation.

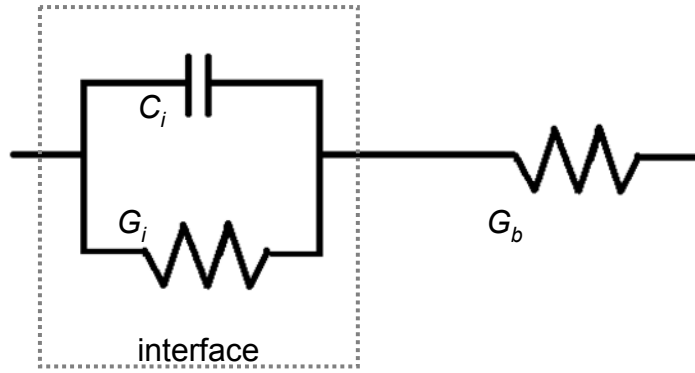


Figure 3.5. Circuit diagram for possible electrode layer responsible for NC.

It appears that an interfacial phenomenon is an unlikely source for the NC in the fluid. However, in order to be conclusive, an experiment was performed. The standard method of determining if the processes in question are due to interfacial or bulk phenomena is to perform impedance measurements on samples of different thicknesses [7]. The analysis is simple if both G_i and G_b are negligibly small, *i.e.*, with capacitive effects alone. If the processes are bulk phenomena, the impedance will vary with the thickness of the sample. If there are dominant interfacial effects, there will be no change in the impedance, and therefore the capacitance [7]. In the case of large G_i and/or G_b , the analysis is more complicated. In the limit of $\frac{G_i}{G_b} = \frac{R_b}{R_i} \gg 1$, which would be expected here, however, an inverse square thickness dependence from equation (3.7) governs the measured capacitance since the bulk resistance scales with thickness. With this in mind, two almost identical cells, A and B, were created with the sole difference being the distance, d_A and d_B , between the electrodes. High frequency capacitance measurements

indicate that the gap of Cell B is approximately 1.8 times of that of Cell A, where $d_A \approx 0.1$ mm. It should be noted that the NC depends on the dc bias so strongly, *e.g.*, with a rate of 3-6%/V for both its low- ω value and its onset frequency, that it offers a good probe. If the NC originates in the bulk, the ratio $\frac{C_B \cdot d_B}{C_A \cdot d_A}$ will be equal to one only if the electric fields are the same in the two cells. However, if the NC is controlled by electrode reactions, then two limits determine the ratio of $\frac{C_B}{C_A}$, with C_A and C_B being the low- ω limits of NC for cells A and B, respectively. If $G_i \ll G_b$, then one would expect $\frac{C_B}{C_A} = 1$ when both cells are under the same bias. In the opposite limit, $G_i \gg G_b$, based on equation (3.7), $\frac{C_B}{C_A} = \left(\frac{d_a}{d_b}\right)^2$ for equal values of the electric field. Cell B was measured under various biases U and compared with the Cell A data at 50 V. The $\frac{C_B}{C_A}$ is only 0.09 with $U = 50$ V, *i.e.*, ten-times lower than that expected for the electrode effects with $G_i \ll G_b$ (Figure 3.6a). The interpolated $\frac{C_B \cdot d_B}{C_A \cdot d_A} = 1.2$ under the same field with $U = 90$ V, on the other hand, is in rough agreement with that expected from the bulk effects, but different from the value of 0.5 that is expected for electrode effects in the $G_i \gg G_b$ limit. The $C(\omega)$ of Cell B at a slightly higher $U = 100$ V, in addition, is almost the same as that of Cell A. The dispersions of the two cells at the same dc bias, however, are very different (Figure 3.6b). Thus, the electric field, as opposed to the voltage, determines the measured value of the capacitance.

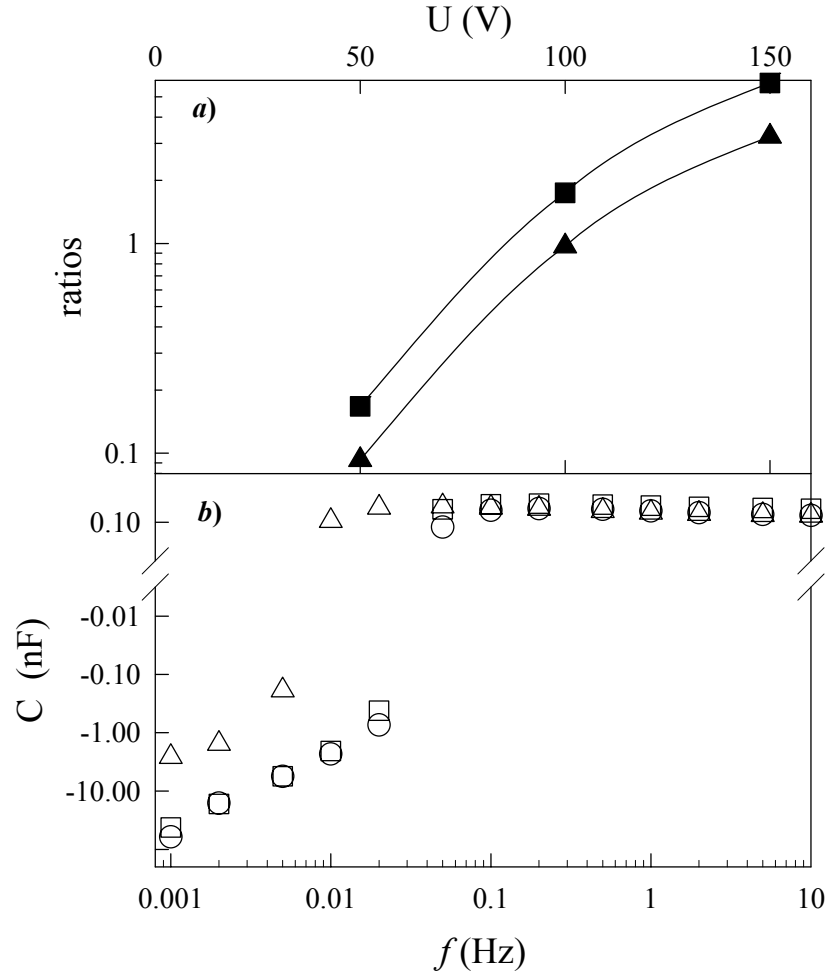


Figure 3.6. a) The ratios $\frac{C_B \cdot d_B}{C_A \cdot d_A}$ (■) and $\frac{C_B}{C_A}$ (▲) at 2 mHz. The dc bias voltages are 50 V and U for the cells A and B, respectively. b) The C of Cell A at 50 V (O), Cell B at $U = 50$ V (Δ) and 100 V ($\square$).

The data, therefore, demonstrate that the NC observed here is a bulk phenomenon. Thus, the ER fluid is linear in the small signal limit and has an off-phase

current that originates in the bulk of the fluid. Therefore, it is natural to associate the resulting NC with a differential dielectric constant.

3.4 Polarity Dependence

The NC exists only in the presence of a *dc* bias. Apart from any anisotropy created by this bias, the fluid is a homogeneous mixture of the nanoparticles and oil. Thus, one would expect that the NC of the fluid should be independent of the sign of the bias. However, this is not guaranteed. There are many examples of polarity dependent NC in the literature. Often, and unsurprisingly, this occurs in diode samples and devices. The ER fluid, however, was found to have a capacitance (positive and negative) that was independent of the bias polarity. Figure 3.7, as an example, shows this effect on the dielectric constant.

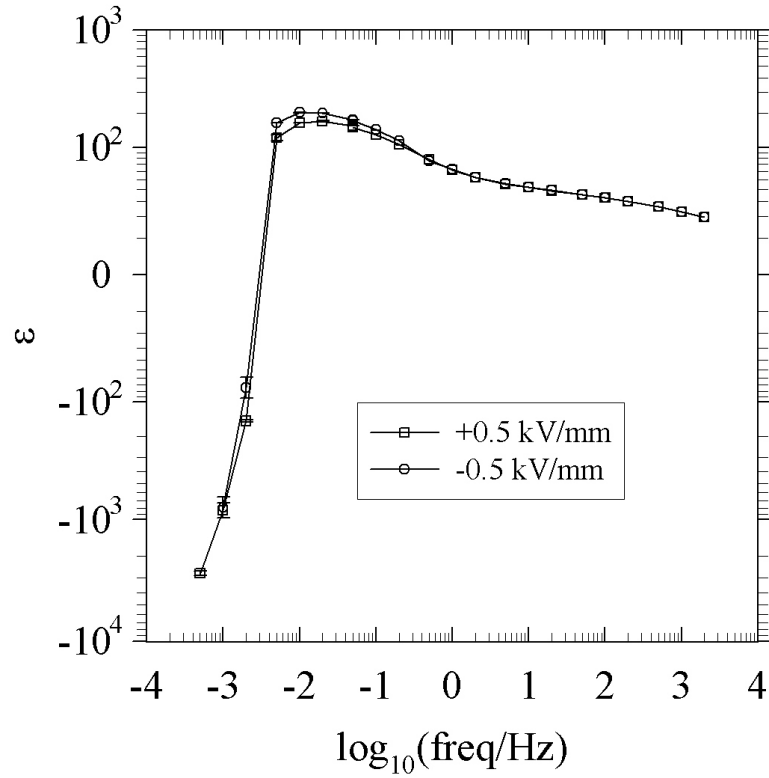


Figure 3.7. Dielectric constant of the fluid for fields of $E = \pm 0.5$ kV/mm. It is clear that the NC is independent of the sign of the dc field.

3.5 Current Flow and Charge Accumulation

In Section 3.2, the time dependence of the current after a step function excitation was examined. The interesting, and somewhat surprising, results allowed for a deeper analysis of the fluid's NC than a frequency domain investigation alone. Similarly, one can study the time dependent current due to a sinusoidal excitation. This is essentially what is done during frequency domain experiments of the type presented in the beginning of this chapter. In that case, the excitation amplitude was small and the

resulting amplitude and phase of the current were the key parameters. If, however, the excitation amplitude is large, the nature of the current flowing through the material can provide some additional insight. In order to study the NC in this manner, the effects due to the resistive and capacitive components of the fluid need to be isolated. This is easily achieved through the I-V loop method described in Section 2.6. The method yields a current vs. voltage graph resembling a loop, *e.g.*, Figure 2.8a. The direction that this loop is traced in time divulges the sign of the capacitance. Moreover, with a large amplitude *ac* excitation and zero *dc* bias, the current (and loop) will change direction at the voltage which generates a sign change of the capacitance. The resistive and capacitive components can be separated by averaging the voltage increasing and voltage decreasing sections of the loop. This average represents the resistive contribution, while the capacitive contribution can be calculated by subtracting the resistive current from the total current.

An experiment of this type was performed on the ER fluid. A 1 mHz excitation with a 200 V peak to peak amplitude was applied to the sample. The resulting current is shown in Figure 3.8a. The capacitive contribution, found after subtracting the resistive contribution from the total, is displayed in Figure 3.8b. One can see three distinct loops, a small central loop, and two outer loops that appear with a larger magnitude of voltage. Arrows indicate the direction of the trace. The central loop is traced in a clockwise direction indicating that the capacitance is positive. Conversely, the outer loops are traced counterclockwise demonstrating that the capacitive is negative in these regions. It should be noted that performing the same experiment at 1 Hz results in a single loop

traced in the clockwise (positive) direction. Another method of presenting the data in Figure 3.8b is by plotting it against time (Figure 3.9).

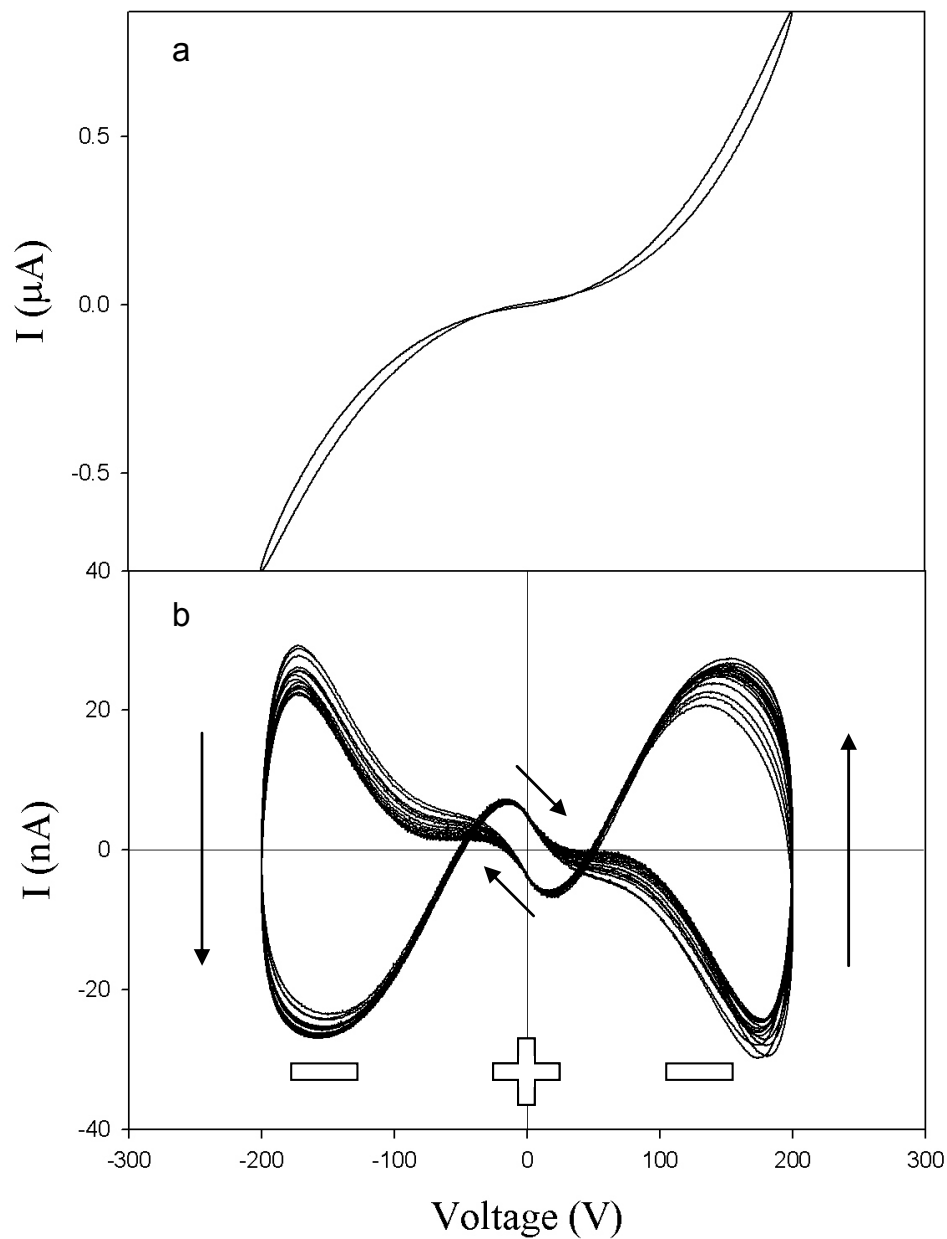


Figure 3.8. a) Total I-V loop from one complete cycle. b) Capacitive current from a. The inner loop is a region of positive capacitance while the outer loops represent NC regions.

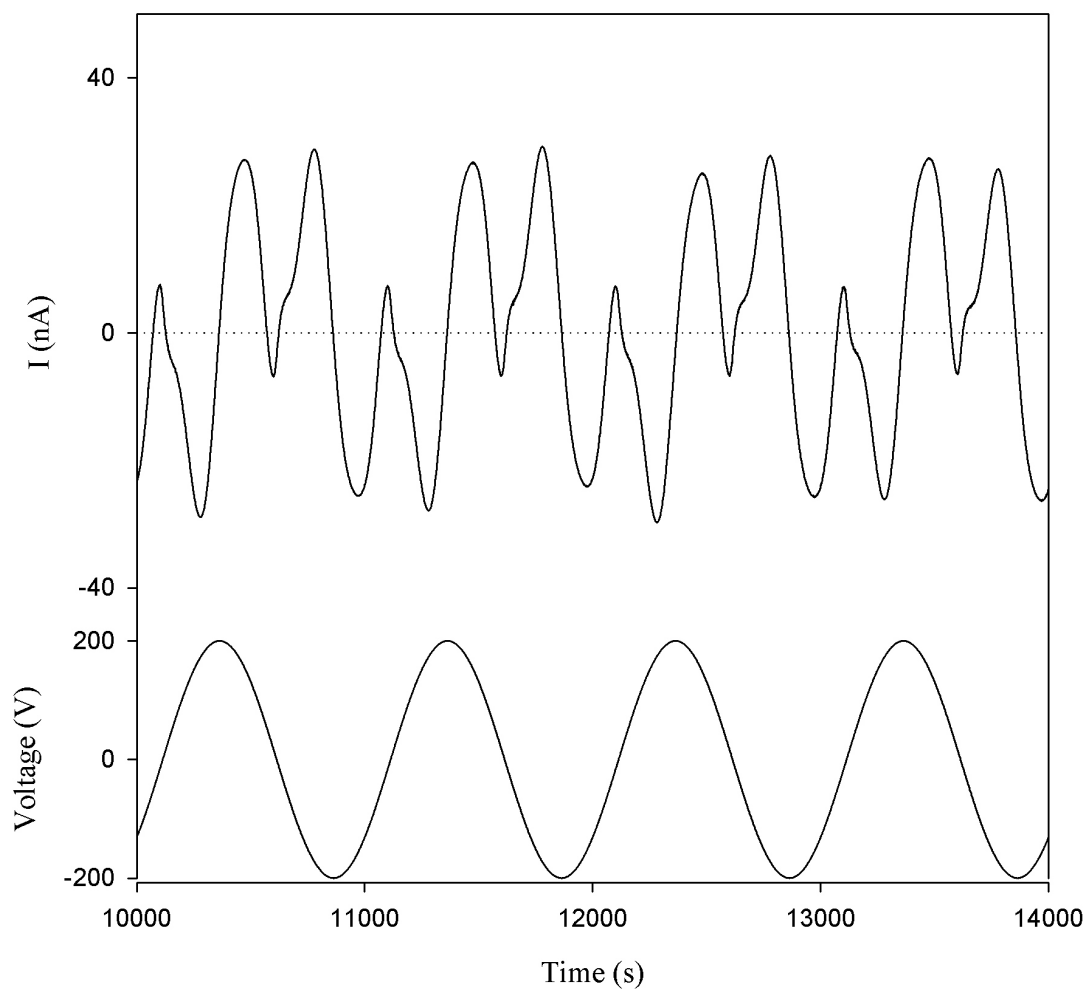


Figure 3.9. Current from Figure 3.8b plotted against time. The excitation voltage is shown below.

This type of behavior is consistent with what is observed in the frequency domain, with the capacitance transitioning from positive to negative values as the voltage is increased. This can be seen in Figure 3.10, in which the dielectric constant, measured at 20 mHz, is plotted against the applied field with the capacitive current from Figure 3.8b superimposed.

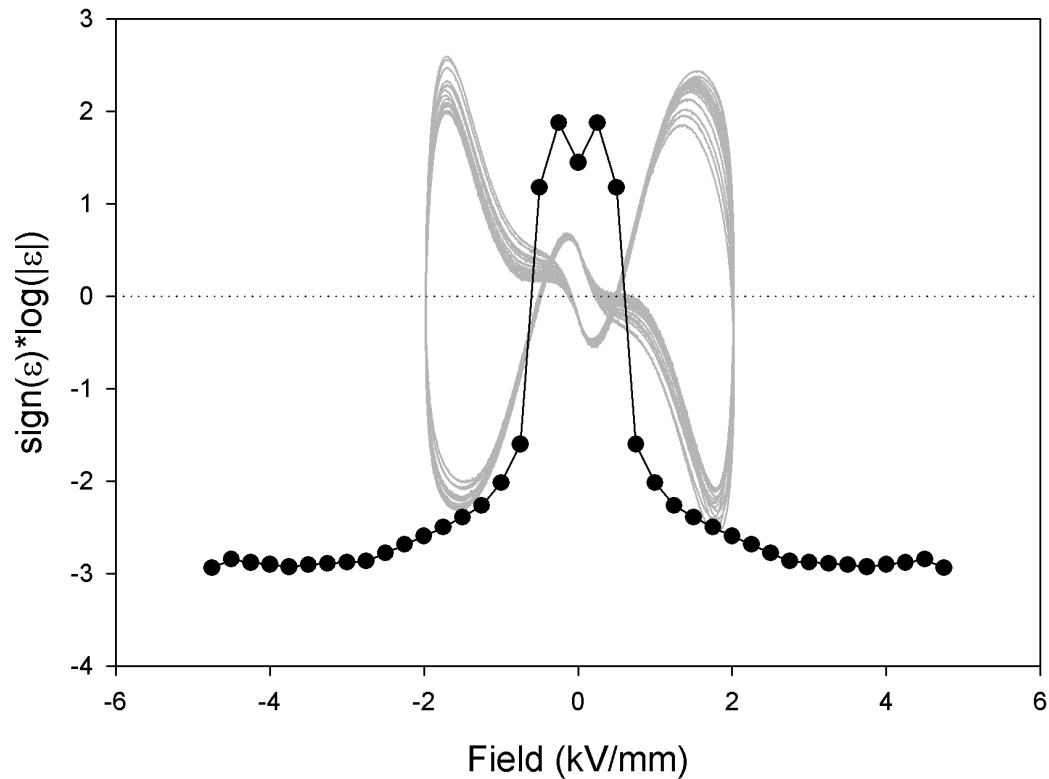


Figure 3.10. Dielectric constant vs. electric field at 20 mHz. The dielectric constant changes sign at roughly the same field at which the trace changes direction. The data points for negative fields were not measured and are for display purposes only.

The field at which the dielectric constant changes sign corresponds roughly to the point where the trace changes direction. A close examination reveals that the dielectric constant changes sign at a slightly higher field than the trace. This is simply due to sample differences and different measurement frequencies. Recall that the loop data were measured with a 1 mHz excitation while the dielectric constant data were taken at 20 mHz. From Figure 3.1, it is clear that higher frequencies require larger fields in order to obtain negative values of the dielectric constant.

This time dependent behavior can once again be predicted by the frequency data.

As discussed in Chapter 2, the current, $I(t) = \frac{dQ}{dt} = \frac{d}{dt}CV$. Expanding the derivative

$$I(t) = C \frac{dV}{dt} + V \frac{dC}{dV} \frac{dV}{dt}. \quad (3.8)$$

If the capacitance is constant, only the first term exists. This is the familiar equation from electronics describing the current due to a capacitor. For large amplitude *ac* excitations, the capacitance of the ER fluid is voltage, and thus time, dependent (Figure 3.8). In this case, the second term in (3.8) is required as well. C and $\frac{dC}{dV}$ estimates can be obtained from the data in Figure 3.10. The voltage is provided in the experiment, so it and its derivative are known. With these parameters and equation (3.8), the time dependent behavior can be determined. This is shown in Figure 3.11.

By comparing Figures 3.8b and 3.9 with Figure 3.11, one can see that that the calculation yields the general features of the data. Some fine details are absent from the calculation. Again, this is due to sample to sample variation and the different measurement frequencies.

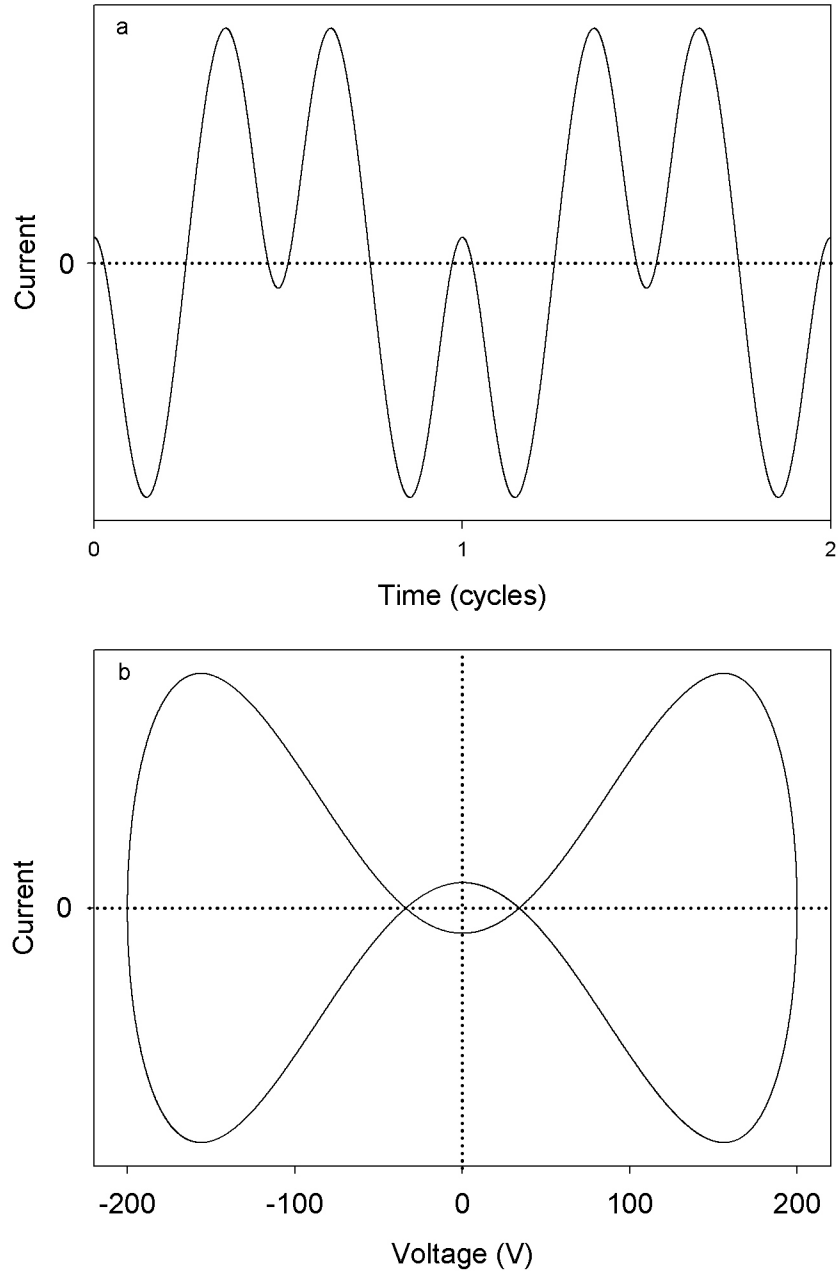


Figure 3.11. Calculation of the time dependent current plotted against time (a) and voltage (b). The voltage dependence of the capacitance was obtained from data in Figure 3.10. Similar behavior was observed in experiment (Figures 3.8b and 3.9).

The current shown in Figure 3.9 can be integrated with respect to time to obtain the charge accumulated across the sample. Since the current under consideration is only the capacitive component, the calculated charge does not include the carriers that passed through the resistive channel. Thus, this calculation yields only the charge associated with polarization and not that which contributes to loss. This is displayed in Figure 3.12.

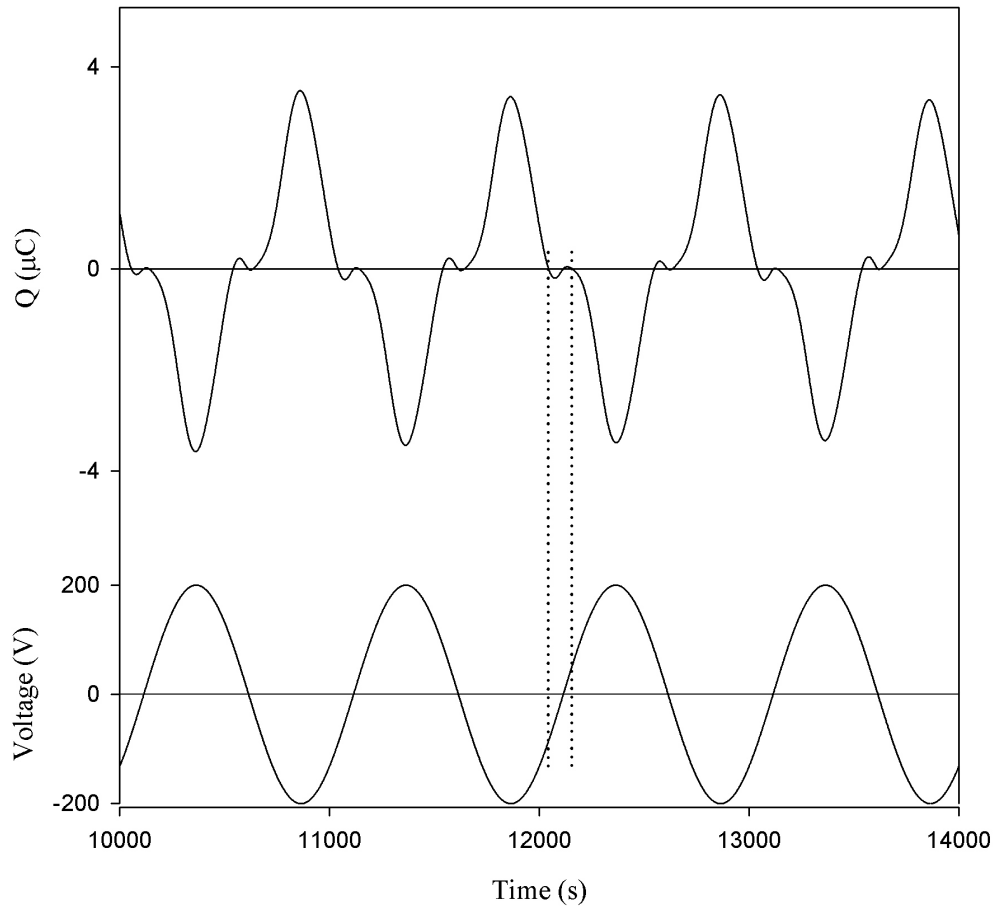


Figure 3.12. Accumulated charge due to integration of $I(t)$. At low voltages, the charge has the same sign as the voltage. At larger voltages, the sign of the charge is opposite.

At low voltages, the charge and the voltage have the same sign. This changes as the magnitude of the voltage is increased. Moreover, the vast majority of charge accumulated during a cycle is negative, *i.e.*, in the sense of $Q = CV$. This is certainly unusual, but not necessarily so unexpected when considering the results of the time domain investigation in Section 3.2 or, more specifically, Figure 3.4. Thus, the data demonstrate that the NC not only changes the sign of the off phase admittance but also that of the accumulated charge. This behavior, therefore, closely resembles that of a material with a negative dielectric constant.

Baseline shifts that occur over the long measurement times complicate any further analysis. Nevertheless, the significant result is that the accumulated charge and, thus, the polarization of the ER fluid is negative at large biases.

3.6 Plasma Response

In the beginning of the chapter it was stated that, due to the analyticity of the admittance, a plasma-like dispersion of the capacitance must be reflected in the resistance. Furthermore, it was argued that the dip which occurs in $1/R(\omega)$ is the natural result of a low frequency plasma-like conductivity, given by equation (3.3), combined with a UDR dispersion at high frequencies. This section will provide a more complete analysis of the plasma-like nature of the admittance.

Consider a material with a plasma-like admittance, *i.e.*,

$$G(\omega) = \frac{1}{R(\omega)} = C_o \frac{\omega_p^2 \gamma}{\omega^2 + \gamma^2}, \quad (3.9)$$

$$C(\omega) = C_o \frac{-\omega_p^2}{\omega^2 + \gamma^2}. \quad (3.10)$$

It has been demonstrated that (3.10) describes the behavior of the ER fluid rather well. If a step excitation is applied to such a material at $t = 0$, a time dependent transient current will be created in both the conductive and capacitive channels, *i.e.*, $\Delta I_Y(t) = I_Y(t) - I_Y(\infty)$ with $Y = G, C$. The total transient current that is generated and dissipated within each channel is simply

$$\Delta I_Y = I_Y(0^+) - I_Y(\infty). \quad (3.11)$$

In other words, the total transient current in each channel is the difference between the currents at short and long times. In the G channel, this can be calculated by

$$\Delta I_G = \Delta V \left(\frac{1}{R_{\omega=\infty}} - \frac{1}{R_{\omega=0}} \right) = -\Delta V C_o \frac{\omega_p^2}{\gamma}. \quad (3.12)$$

where $\omega = \infty$ and 0 correspond to short and long times, respectively. In (3.12), the second equality is obtained using equation (3.9). In the C channel, the transient current can be calculated using

$$\Delta I_C = \frac{2}{\pi} \Delta V \int_0^\infty [C(\omega) - C(\infty)] d\omega = -\Delta V C_o \frac{\omega_p^2}{\gamma}. \quad (3.13)$$

which was derived in Ref. 10 from a frequency dependent capacitance alone.

From equations (3.12) and (3.13) it is clear that each channel contributes equally to the total transient current in the material such that

$$\Delta I_{tot} = \Delta I_G + \Delta I_C = 2\Delta I_G. \quad (3.14)$$

For a true plasma response, (3.14) must hold. It will provide a nice test for plasma behavior in the ER fluid. This relationship can be verified by measuring the total transient current as well as the low and high frequency limits of the resistance (see equation (3.12)). A method to measure the total transient current has already been described in Section 3.2. The resistance values can be measured using the I-V loop method of Section 2.6.

In order to obtain the total transient current, a series of ± 10 V step excitations were superimposed on 350 V *dc* bias at 1032 s intervals. The time dependent transient current after a jump from 350 to 340 V is shown in Figure 3.13. As in Figure 3.4, the transient current changes sign after 1-2 ms (not apparent due to scale). However, the negative ΔV results in a positive transient current (see equations (3.12) and (3.13)). The total transient current due to the plasma component is calculated as the difference between the value after the high frequency, positive components dissipate and the final (long time) value. One can see from Figure 3.13 that the total transient current obtained during a jump from 350 V to 340 V is approximately 0.15 μA .

The I-V loop method was used to measure the transient current in the conductive channel. Equation (3.12) indicates that it is necessary to measure the difference between the currents in the high and low frequency limits. In practice, the frequency range need not be so extreme, as demonstrated by Figure 1.2, which shows that the conductivity is frequency independent for both large and small ω and varies with frequency in a relatively narrow range. In fact, the upper limit of the plasma behavior is restricted due to the presence of UDR behavior above 1 Hz. Thus, for experimental purposes, the high and low frequency plasma behavior will be measured at 0.3 and 0.001 Hz, respectively.

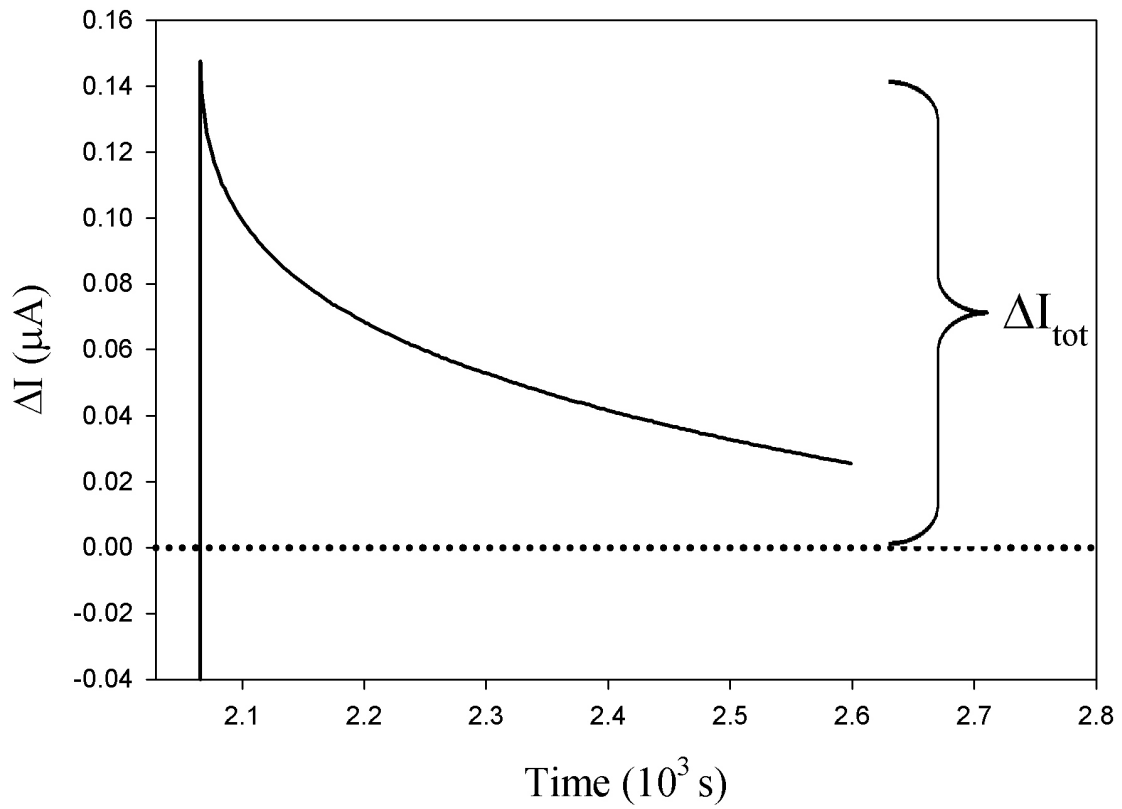


Figure 3.13. Transient current resulting from a 350 to 340 V jump. The total transient current measured is approximately 0.15 μA .

In order to achieve conditions similar to that of the total transient current measurement described previously, 20 V peak to peak *ac* excitations were superimposed on a 350 V *dc* bias. The conductive component can be isolated from the resulting I-V loops by averaging the voltage increasing and decreasing branches of the loop (see Section 2.6). The results, for loops with frequency 0.3 and 0.001 Hz, are displayed in Figure 3.14.

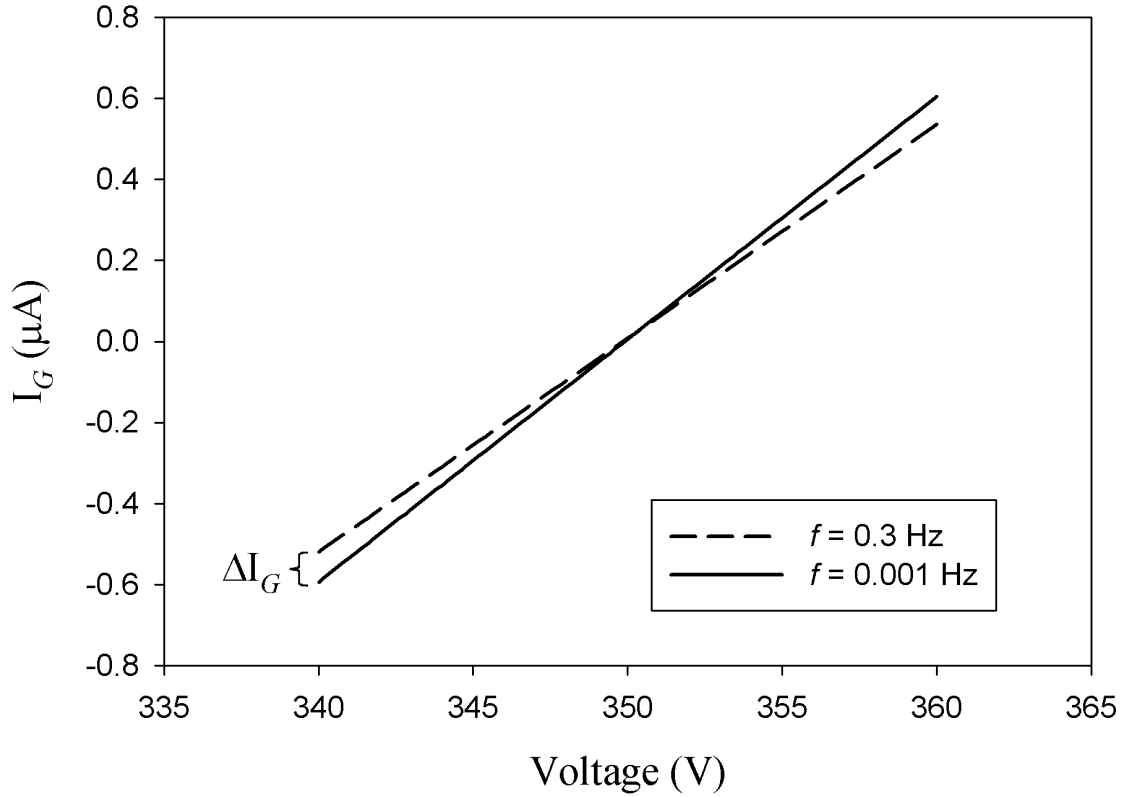


Figure 3.14. Current flowing through the resistive channel of the ER fluid obtained from I-V loops. The difference between the high (0.3 Hz) and low (0.001 Hz) frequency currents is $\Delta I_G = 0.074 \mu\text{A}$.

The two $I_G(V)$ curves shown in Figure 3.14 have different slopes. This implies that the resistance is frequency dependent. Recall that this was not discernable in Figure 3.1. The resulting ΔI_G can be calculated by subtracting the 0.3 Hz curve from the 0.001 Hz curve. At 340 V, ΔI_G is approximately $0.074 \mu\text{A}$. This, combined with the measured ΔI_{tot} of $0.15 \mu\text{A}$, indicates that equation (3.14) is satisfied. Thus, the plasma component, which was obscured in the impedance data, is observed in the resistance of the ER fluid. Moreover, this demonstrates that the ER fluid exhibits a true plasma-like response.

3.7 Effect of Temperature

All of the experiments described thus far have been performed at room temperature. Similar measurements have also been completed both above and below the ambient temperature in the laboratory. This section will examine the effect of temperature on the resistance and capacitance of the ER fluid.

Experiments at elevated temperatures were performed in an environment designed to generate a stable, uniform temperature for the ER fluid samples. An aluminum block was machined to accommodate the glass vial that housed the sample. This block was embedded in foam insulation, and a thermoelectric element was attached, via heat sink compound, to the outer face. A heat sink was affixed, by the same method, to the other side of the element. The vial, with an ample amount of heat sink compound, was inserted into the block. A temperature controller was used to drive the thermoelectric element while the temperature was read by a temperature sensor mechanically connected to the aluminum block.

Temperatures of 0° C were obtained by simply immersing the vial in an ice/water mixture.

The dielectric constants of two ER samples, one at room temperature (RT) and the other at 50° C, are shown in Figure 3.15. While UDR-like behavior is observed at both temperatures with $V_{dc} = 0$, increasing the temperature has the effect of increasing the low frequency dielectric constant. With a dc bias of 50 V, the dielectric constant at 50° C changes sign at a higher frequency and becomes more negative than the RT value.

Thus, increasing the temperature has the effect of enhancing the magnitude of the dielectric constant, $|\varepsilon|$, regardless of the value of the bias. This, combined with the increase in the transition frequency, demonstrates that the over all NC effect is enhanced as the temperature is raised. It should be noted that, while sample to sample differences can exist, they are not able to account for the dramatic enhancements displayed in Figure 3.15.

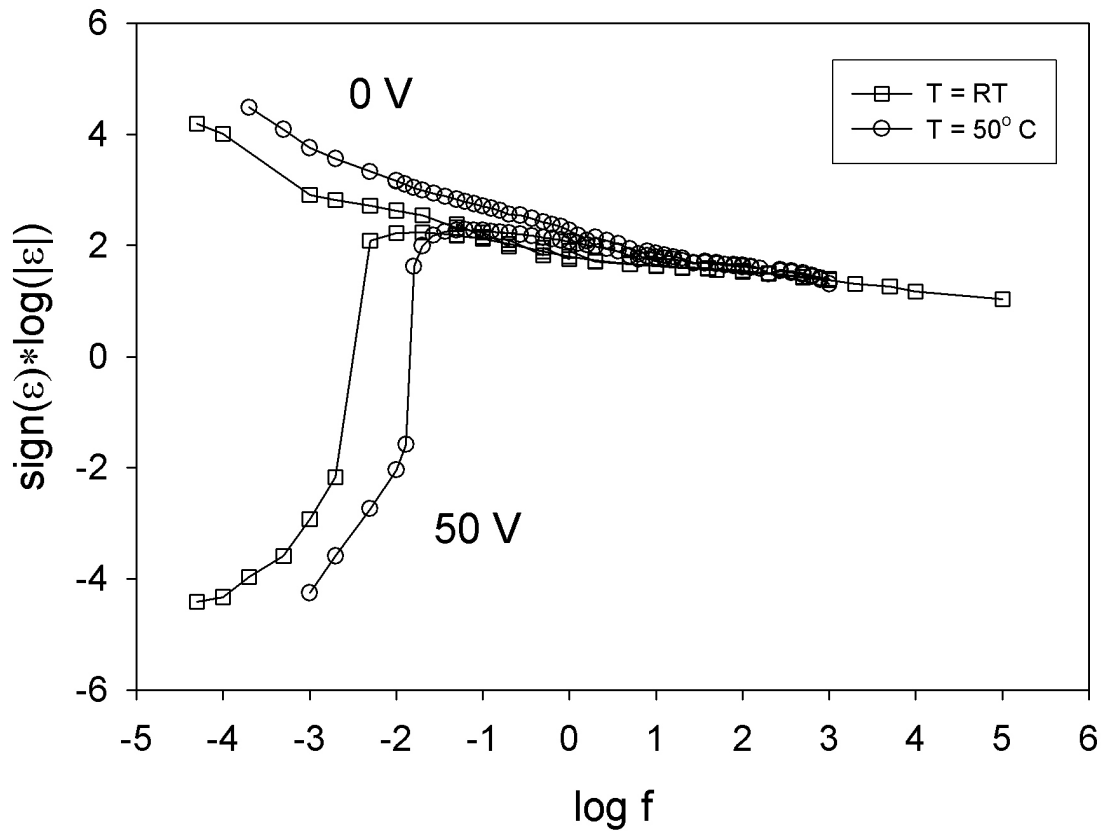


Figure 3.15. The dielectric constants of two ER fluid samples at room temperature (RT) and 50°C . The increase in temperature results in an enhancement of the magnitude of the dielectric constant as well as an increase in the frequency at which the dielectric constant changes sign.

Conversely, cooling the ER fluid drastically suppresses the NC. This effect can be seen Figure 3.16, which shows the dielectric constant of a sample at RT and 0° C with a bias of 200 V. At 0° C, NC is almost unobservable within the frequency range of the experiment. The transition to negative values occurs between 1 and 2 mHz. The value at RT is more than an order of magnitude larger.

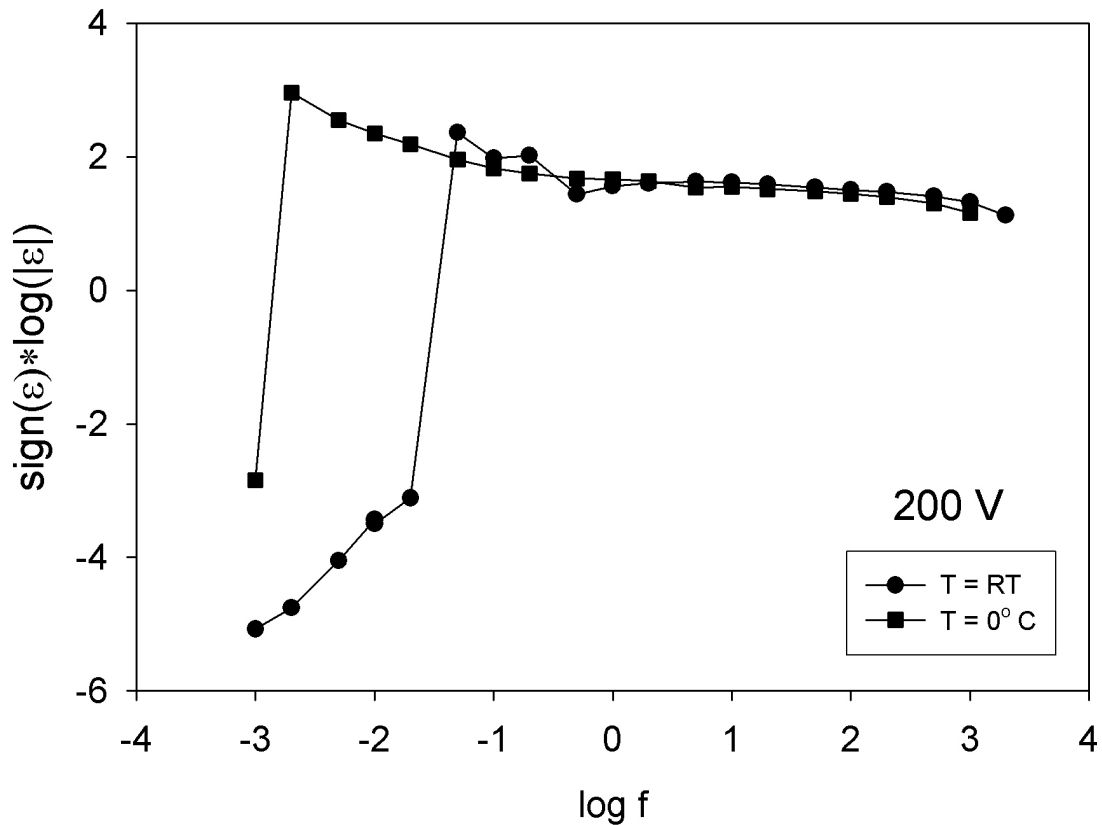


Figure 3.16. The dielectric constant of an ER fluid at 0° C and RT. Cooling suppresses the NC.

Finally, the effect of temperature on the resistance should be mentioned. As one might expect, the resistance decreases as the temperature is increased.

3.8 Pellet Samples

The experiments described throughout this chapter have been performed exclusively on ER fluid samples. However, as mentioned in Chapter 2, pellets made from the nanoparticles used in the fluid have been fabricated and studied. Recall that the ER fluid consists of urea-coated $\text{Ba}_{0.8}\text{Rb}_{0.4}\text{TiO}(\text{C}_2\text{O}_4)_2$ nanoparticles immersed in a low viscosity silicone oil. The pellets were created by cold pressing the nanoparticles between indium electrodes.

The purpose of such an investigation was to examine the effect that nanoparticle motion might have on the NC. The ER fluid is unique in two ways. It has an unusually strong ER effect and it exhibits NC. It was thought that the phenomena might be related. By studying nanoparticles confined in a pellet, the effect of large scale nanoparticle motion would essentially be removed.

Like the fluid, the dielectric constant of the pellets is strictly positive and possesses a dispersion similar to the UDR without the presence of a *dc* bias. Upon application of a bias, the dielectric constant strays from the UDR behavior and becomes negative with a plasma-like dispersion. This, again, mirrors the behavior of the fluid. The dielectric constant (and capacitance) of a 0.95 mm pellet under an applied field of $E_{dc} = 0.37$ kV/mm can be seen in Figure 3.17. It should be noted that the NC effect is much stronger in the pellet than in the fluid. The frequency at which the dielectric constant becomes negative is as large as in the fluid at the highest biases. Furthermore, even with the modest frequencies and applied field, the dielectric constant of the pellet in

Figure 3.17 is more negative than any fluid measured during the course of the study.

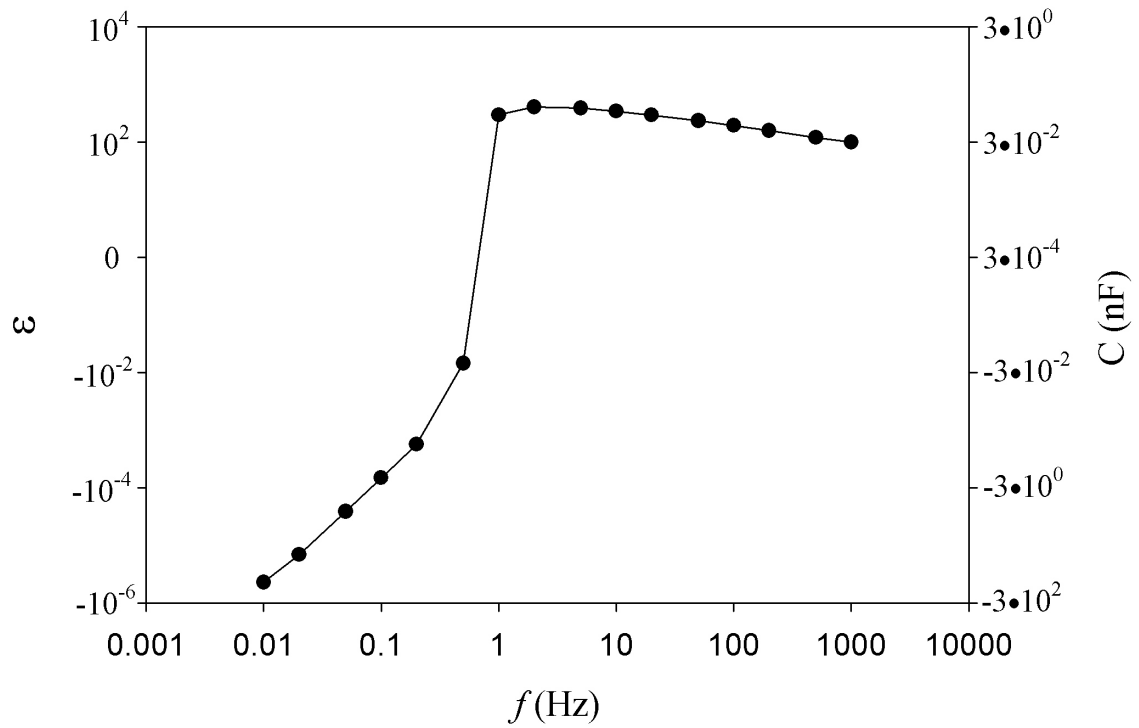


Figure 3.17. The dielectric constant and corresponding capacitance values for a 0.95 mm pellet under and applied bias field of 0.37 kV/mm. The dielectric behavior is similar to the ER fluid.

More noteworthy, however, is the similarity of the pellet and fluid dispersions. This indicates that the silicone oil is not required for the manifestation of NC. Furthermore, the nanoparticles must be responsible for the occurrence of NC in the fluid. This may not be surprising considering the large amount of nanomaterials that exhibit NC. Most significantly, the data in Figure 3.17 reveal that the electrorheological effect is not responsible for the NC in the fluid. Within the pellet, the nanoparticles are

relatively fixed. This is unlike the fluid, where the particles are free to form columns and chains in the presence of an applied bias. The similar dielectric behavior between the pellet and the fluid indicates that large scale particle motion or rearrangement, like that which occurs in the electrorheological effect, cannot be responsible for the NC.

The data in Figure 3.17 were obtained under ambient conditions in the laboratory, *i.e.*, at room temperature and approximate relative humidity of 60-70 percent. Pellets were also measured in dry environments by sealing them in jars containing drierite, a granular desiccant. The effect of the moisture removal is significant, as can be seen in Figure 3.18, which shows the dielectric constant of a 1.5 mm pellet that had been in the dry environment for approximately two days. The dielectric constant of the dry pellet is positive across the entire frequency range for all biases applied. The fields subjected to the dry pellet were not as large as those applied to the pellet measured in the ambient environment (0.233 compared to 0.37 kV/mm); however, they were certainly large enough to produce a transition to negative values since the minimum field required to generate NC in the fluid is approximately 0.15 kV/mm. There is a slight downturn of the dielectric constant at the lowest frequencies and highest bias in Figure 3.18 which could be an indication of the onset of NC. However, it is clear that the removal of the moisture significantly suppresses the transition to negative values.

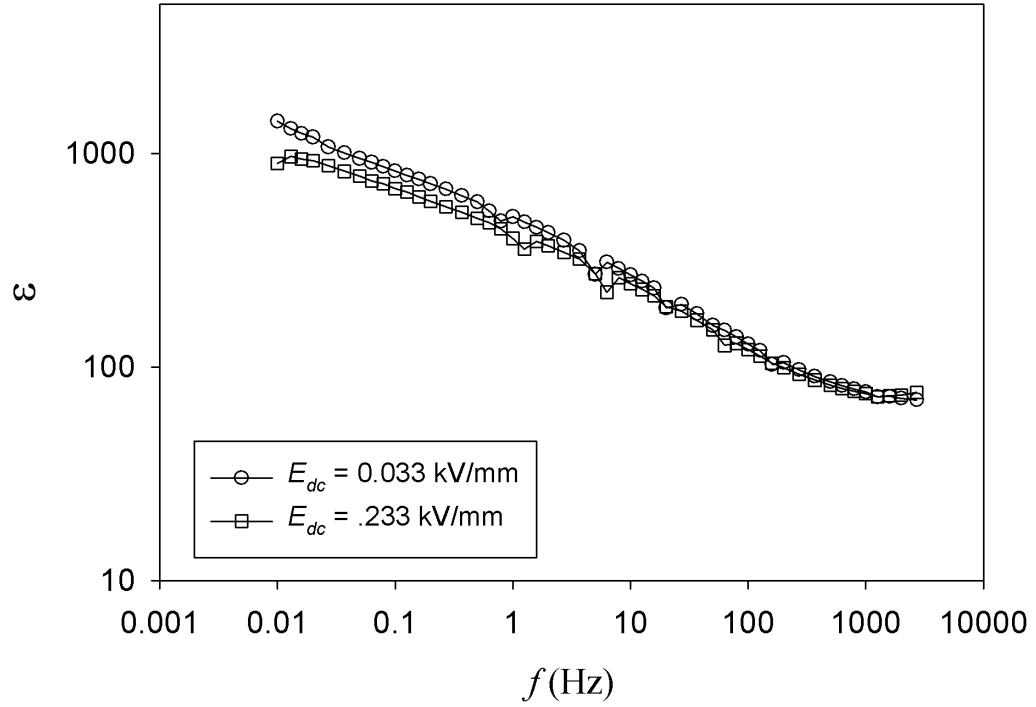


Figure 3.18. The dielectric constant of a pellet in a dry environment at various biases. Unlike the pellet in ambient conditions, the dielectric constant is positive.

Unsurprisingly, the moisture removal also has a significant effect on the resistance. Figure 3.19 shows the zero-bias resistance of the pellet, from Figure 3.18, measured after approximately 2 days and 1.5 months. After 2 days in the dry environment, there are features in the dispersion of the resistance. These features are absent after 1.5 months of drying, and the frequency dependence has converted to a typical UDR dispersion, which is similar to the fluid and what one would expect for a disordered material. Furthermore, with the continued drying comes a significant enhancement of the resistance.

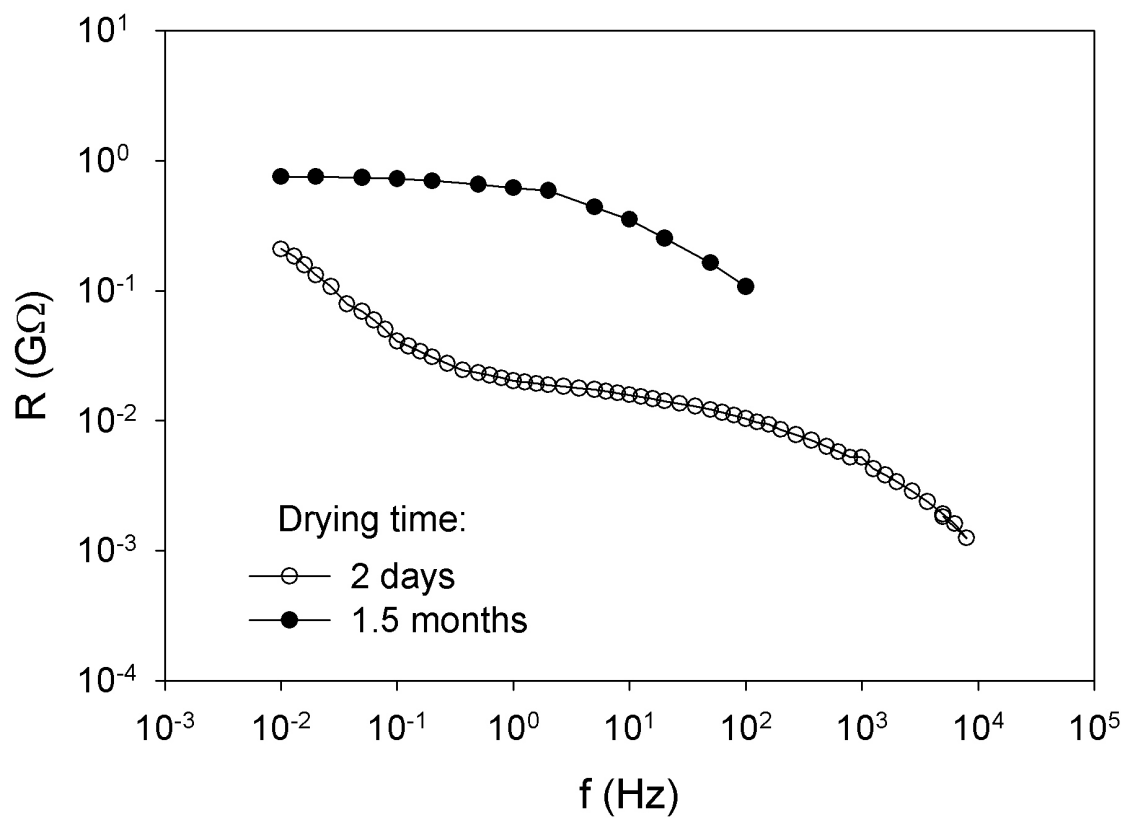


Figure 3.19. The resistance of pellet at two stages of the drying process. The frequency dependent features give way to a UDR dispersion as the drying progresses. The resistance is significantly enhanced as the moisture is removed.

3.9 General Remarks

This chapter, while not comprehensive, has presented the key results from this study. Almost no mention has been made to the mechanism responsible for the NC observed in the ER fluid or pellet. This has been reserved for the following chapter. However, to conclude the present one, some brief remarks will be made.

Previously, it was stated that ER effect cannot be responsible for the NC since large scale particle rearrangements cannot be present in the pellet. The similarities in the dispersions of the ER fluid and pellet indicate that the nanoparticles are responsible for the NC. Therefore, the silicone oil is not a key component.

During the course of this chapter, much characterization of the NC has been performed. Of particular importance were the observations that the NC of the ER system was enhanced under three conditions: *i*) an increase in voltage, *ii*) an increase in temperature, and *iii*) an increase in moisture content. Furthermore, it was shown that these three conditions all serve to increase the conductivity of the material. Thus, it appears that the conductivity is a fundamental factor in determining the NC of the material. In particular, the response of the pellet to moisture indicates that the nanoparticle surface conductivity is the important parameter since the moisture most likely resides on the surface of the particles or in the thin urea layer.

The connection between NC and the conductivity is supported by Figure 3.1 where, at the highest biases, the NC becomes bias independent as the conductivity becomes less sensitive to bias. A more detailed description of the relationship between

the bias and conductivity, as it pertains to the NC, will be presented in the next chapter. Further evidence is provided by Figure 3.2, which shows that there is an enhancement in the nonlinearity of the conductance when the capacitance becomes negative. Specifically, at the onset of NC the nonlinearity increases and is maintained to the lowest frequency measured, or, in other words, as long as the capacitance is negative. Thus, it appears that there is a direct correlation between the nonlinearity of the ER fluid and the NC.

3.10 Chapter References

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Chapter 4: A General NC Mechanism

As stated in Chapter 1, NC is not limited to the ER fluid and pellet, but has been observed in many materials and devices spanning all of the major branches of science. Furthermore, it has been shown that NC can originate at interfaces as well as in the bulk of the materials. Naturally, a broad range of physical processes govern the behavior of such a diverse group of systems. This has led to NC being studied on a case-by-case basis in individual materials and not generally as a single phenomenon. Some reports have proposed mechanisms, with varying degrees of rigor, behind the NC for the particular case in question. The explanations of these observances are as varied as the materials in which they are found. Surprisingly, however, many instances of NC share several common features: *i*) they arise in the presence of a *dc* bias, *ii*) the materials have a nonlinear conductance, and *iii*) they possess dispersion. Additionally, many of the systems exhibit very similar manifestations of NC.

From Chapter 3, it is clear that the ER fluid possesses the common features listed above. The NC is only measured in the presence of a *dc* bias. If a bias was not applied, the capacitance was positive across the entire frequency range. The conductivity is nonlinear, and it was shown to have a plasma-like component that was hidden in the original impedance data. Furthermore, among the key conclusions of the chapter was the existence of a distinct relationship between the nonlinearity and the NC.

In this chapter, the above mentioned common features are exploited to demonstrate the basic requirements necessary for NC, and a general mechanism,

appropriate for many instances of NC, is formulated. This mechanism allows one to predict the NC value of the fluid by merely examining the nonlinearity of the conductivity, and thus, confirms the relationship that was identified in Chapter 3. Additionally, the validity of the model will be further demonstrated on published data from an unrelated material, a fuel cell. Thus, seemingly unrelated instances of NC can be united under a common framework.

4.1 Development

By definition, a nonlinear material has a voltage dependent conductance, $G(V)$. This nonlinearity can complicate the analysis of such a material. However, for a dispersionless conductance, the current induced by a voltage can be written as

$$I = G(V) \cdot V. \quad (4.1)$$

The impedance experiments performed to measure NC utilize a small *ac* excitation superimposed on a *dc* bias such that the total voltage applied to the material is $V = V_{dc} + V_{ac} \sin(\omega t)$. In such a case, the total current flowing through the material will be

$$I_{tot} = G(V_{dc} + V_{ac} \sin(\omega t)) \cdot (V_{dc} + V_{ac} \sin(\omega t)). \quad (4.2)$$

The small *ac* excitation acts as a perturbation from V_{dc} , and the conductance can be Taylor expanded about the *dc* level to obtain, in the small signal limit,

$$G(V \sim V_{dc}) \approx G(V_{dc}) + \left. \frac{\partial G}{\partial V} \right|_{V_{dc}} (V - V_{dc})$$

or

$$G(V \sim V_{dc}) \approx G(V_{dc}) + V_{ac} \sin(\omega t) \left. \frac{\partial G}{\partial V} \right|_{V_{dc}}. \quad (4.3)$$

Keeping terms to first order in V_{ac} results in a total current of

$$I_{tot} \approx V_{dc} G(V_{dc}) + V_{ac} \sin(\omega t) G(V_{dc}) + V_{dc} V_{ac} \sin(\omega t) \left. \frac{\partial G}{\partial V} \right|_{V_{dc}}. \quad (4.4)$$

The first two terms in equation (4.4) represent, in a linear system, the dc and ac currents, respectively. The presence of any nonlinearity in G results in the third term, which is a consequence of mixing the dc and ac signals. In fact, the third term can be thought of as another ac current, *i.e.*,

$$I_1 = \left(V_{dc} \left. \frac{\partial G}{\partial V} \right|_{V_{dc}} \right) V_{ac} \sin(\omega t). \quad (4.5)$$

Note that this term, like the other ac current, is linear in V_{ac} even though it arises due to the nonlinearity of the conductance. This is a consequence of the material being measured in the small signal limit. The factor in parenthesis can be regarded as a conductance:

$$G_1 = V_{dc} \left. \frac{\partial G}{\partial V} \right|_{V_{dc}}. \quad (4.6)$$

The ac current in equation (4.4) can be written as

$$I_{ac} = \left(G(V_{dc}) + V_{dc} \left. \frac{\partial G}{\partial V} \right|_{V_{dc}} \right) V_{ac} \sin(\omega t) \quad (4.7)$$

or, upon rearrangement,

$$\frac{I_{ac}}{V_{ac} \sin(\omega t)} = G(V_{dc}) + V_{dc} \left. \frac{\partial G}{\partial V} \right|_{V_{dc}}. \quad (4.8)$$

The left hand side of (4.8) is the value measured during an impedance experiment, and is, by definition, $\frac{1}{R_{ac}}$. Thus, the total differential conductance is then

$$\frac{1}{R_{ac}} = G_0 + G_1, \quad (4.9)$$

where $G_0 = G(V_{dc})$. The nonlinearity results in the inclusion of G_1 instead of, simply, the zero order conductance $G_0 = G$, as expected in linear systems.

The equations derived above are exact for the case of a dispersionless conductance and offer a good approximation if the frequency dependence is weak. Fortunately, most materials usually possess only minor dispersions at low frequencies in the conductance channel, where NC commonly arises. Thus, in a frequency region relevant to the study of NC, equations (4.1) - (4.9) will typically remain valid and can be applied to actual experimental data. The presence of any frequency dependence will have the effect of shifting G_1 away from the dispersionless-limit of $V_{dc} \frac{\partial G}{\partial V}$. However, this modified G_1 will still be associated with the modulation of the dc bias through the overall voltage dependent conductance.

G_1 will be referred to as the modulation conductance. Many known modulated currents, such as I_1 in (4.5), are retarded against the applied voltage, *e.g.*, minority carrier migration across a depletion layer or delay due to poisoning (contamination) of electrodes. Such retarded currents, however, are exactly the same *ac* responses to an inductor or a capacitor with $C < 0$. Mathematically, the retarding of current is equivalent

to adding a complex phase factor, *i.e.*, changing the real $V_{dc} \frac{\partial G}{\partial V}$ into a complex admittance $A_1 = |A_1| e^{-i\theta}$ such that $\text{Re}[A_1] = V_{dc} \frac{\partial G}{\partial V}$. The capacitance that is responsible for the phase shift is

$$C_1 = -V_{dc} \frac{\partial G}{\partial V} \frac{\tan \theta}{\omega}. \quad (4.10)$$

The total capacitance, which is the sum of a geometric capacitance C_0 and C_1 from (4.10), will be negative if

$$V_{dc} \frac{\partial G}{\partial V} > \frac{C_0 \omega}{\tan \theta} > 0. \quad (4.11)$$

Simply put, the nonlinearity and the *dc* bias combine to add an additional term to the *ac* current, which quite often lags behind the voltage. This retarded current is manifested as a negative contribution to the capacitance. A negative capacitance appears when this contribution (equation (4.10)) becomes dominant. The requirements of the mechanism are very general. However, a host of microscopic phenomena can produce the above mentioned effects, thus explaining the wide array of materials that exhibit NC.

To verify the idea experimentally, however, one still needs to formulate it such that C_1 can be directly deduced from the measured modulated conductance G_1 . Writing the frequency dependence explicitly,

$$G_1 = V_{dc} \left. \frac{\partial G}{\partial V} \right|_{\omega=0} F'(\omega), \quad (4.12)$$

where $F'(\omega)$ is the real part of a complex function describing the dispersion of the nonlinearity. In most practical cases, the complex admittance, A_1 , is an analytic

(holomorphic) function, *i.e.*, fully differentiable against ω [1]. Thus, the corresponding contribution from the capacitance,

$$C_1 = V_{dc} \left. \frac{\partial G}{\partial V} \right|_{\omega=0} \frac{F''(\omega)}{\omega}, \quad (4.13)$$

can be calculated from G_1 by solving the Cauchy-Riemann equations for $F''(\omega)$. This is the most general representation of the mechanism. From equations (4.12) and (4.13), one can see that a material with a dispersive nonlinearity, in the presence of a dc bias, will have an additional capacitance contribution which has a frequency dependence that is described by the imaginary counterpart of $F'(\omega)$. In general, the sign of this contribution can be either positive or negative.

The relationship between G_1 and NC can be seen more clearly for the specific case of a plasma-like dispersion. In such a case, the modulation conductance is

$$G_1 = V_{dc} \left. \frac{\partial G}{\partial V} \right|_{\omega=0} \frac{\gamma}{\omega^2 + \gamma^2}. \quad (4.14)$$

The contribution to the capacitance associated with this conductance is

$$C_1 = -V_{dc} \left. \frac{\partial G}{\partial V} \right|_{\omega=0} \frac{1}{\omega^2 + \gamma^2}. \quad (4.15)$$

With $\left. \frac{\partial G}{\partial V} \right|_{\omega=0} > 0$, such a term will yield a negative contribution to the capacitance, and

as is often the case, become dominant at low frequencies. The above inequality holds for the ER fluid, as it does for most materials, and the fluid's small γ renders the value in (4.15) rather large. It is clear that, in order to calculate this effect on the capacitance, one only needs knowledge of the material's nonlinearity.

4.2 The Mechanism and ER Fluid

In principle, the mechanism described above should contribute to the capacitance of the ER fluid, since the fluid has a dispersive nonlinearity and is measured in the presence of a dc bias. Whether this effect can be experimentally demonstrated in the fluid or if it is even the dominant NC mechanism, however, is another matter. The key is to determine the frequency dependence of the modulation conductance G_1 without numerically calculating the derivatives over many data subsets at different dc biases. The low frequency conductivity of the ER fluid is highly sensitive to changes in room temperature and the rearrangement of nanoparticles while under bias. Low frequency measurements at various biases can take several weeks to complete. During this period, such effects contribute to conductance drifts which interfere with direct calculation of $\frac{\partial G}{\partial V}$. A new approach based on equation (4.9) has, therefore, been employed to minimize the effects of both the drifts at low frequencies and the residual dispersion of the conductance. G_0 is the expected response of an “equivalent” linear system. At high frequencies, the conductance is voltage independent indicating that the material is linear in this region (see Figure 3.1). Thus, the UDR-like dispersion that exists at high frequencies can be attributed to G_0 . As implied above, NC is not observed in linear systems. As an example, a plasma dispersion in a linear system is essentially the result of Drude behavior. In this case, the value γ represents the carrier collision rate and is typically large. This results in a negligible phase angle and thus, only an in phase conductance, *i.e.*, no measurable capacitance, at low frequencies [2, 3]. Therefore, the

low frequency plasma-like dispersion observed in the fluid is not expected to reside in G_0 . As a result, G_0 is anticipated to be frequency independent in the low frequency region, and the plasma-like dispersion is left to G_1 . This is supported by the enhancement of the nonlinearity, *i.e.*, G_1 , below the frequency at which the capacitance becomes negative (Figure 3.2). The negligible frequency dependence of the linear term allows one to set $G_0 = \frac{I_{dc}}{V_{dc}}$. The nonlinearity can then be approximated, from (4.9), as

$$G_1 \approx \frac{1}{R_{ac}} - \frac{I_{dc}}{V_{dc}}, \quad (4.16)$$

which involves only the concurrently measured R_{ac} and I_{dc} . The effects of the drifts, therefore, are minimized. At high frequencies, the UDR dispersion of G_0 makes the use of (4.16) inappropriate, and the $\frac{\partial G}{\partial V}$ must be calculated numerically. Fortunately, the period needed to measure the high frequency admittances is short, and the drift is negligible.

Figure 4.1a shows the nonlinearity, $V_{dc} \frac{\partial G}{\partial V}$, of the ER fluid at 50 V that was deduced by the method described above for frequencies below 0.1 Hz (circles) and by direct numerical calculation above 10 Hz (triangles).

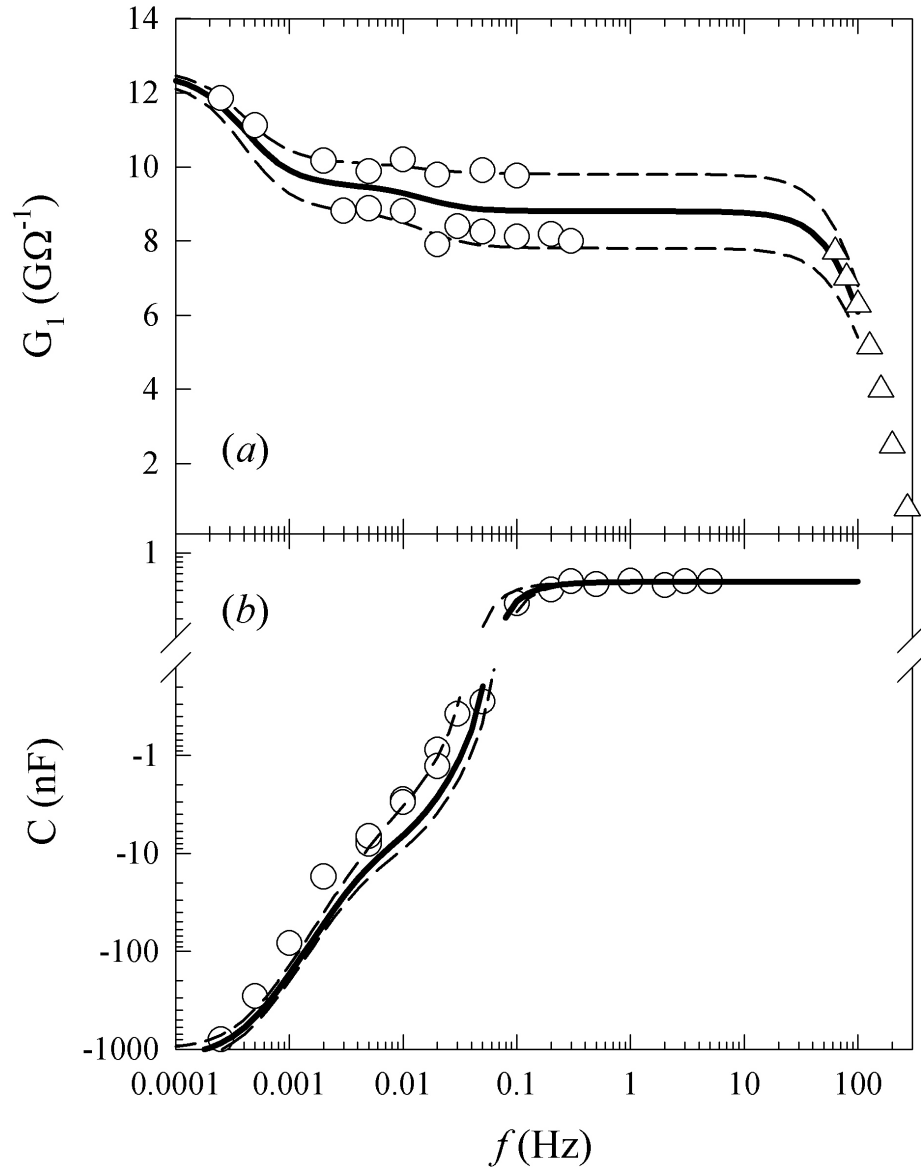


Figure 4.1. a) The modulation conductance (nonlinearity) of the ER fluid at $V_{dc} = 50$ V. The symbols are the measured data, and the lines are fits of three superimposed plasma-like relaxations, which represent the best fit and the upper and lower boundaries. The data scattering is much larger than the repeatability of the measured $1/R_{ac}$ due to the cancellation of $\frac{1}{R_{ac}(\omega)}$ and $\frac{I_{dc}}{V_{dc}}$. This 15% uncertainty, fortunately, still allows a reasonable prediction due to the large dynamic range of C . b) The capacitance under the same conditions. The symbols are the data. The lines are predictions from the model using the nonlinearity deduced in (a).

The nonlinearity was then fit with a series of three plasma relaxations, *i.e.*, as

$$G_1 = \sum_{i=1..3} f_i \frac{a_i}{f^2 + f_i^2} \text{ with } a_i \text{ and } f_i = \gamma_i / 2\pi \text{ as fitting parameters (see equation (4.14)).}$$

Three fits were used. One represents the averaged data (central line), while the others indicate the upper and lower boundaries (outer lines). From equations (4.14) and (4.15), a material with such a nonlinearity must have a capacitance given by

$$C_1 = -\frac{1}{2\pi} \sum_{i=1..3} \frac{a_i}{f^2 + f_i^2} + 5 \cdot 10^{-10}, \text{ where the constant } 5 \cdot 10^{-10} \text{ F represents the high}$$

frequency geometric capacitance (Figure 4.1b). The prediction from the mechanism agrees with the data reasonably well, especially considering the dynamic range of the measured capacitance.

It should be emphasized that a fit for the measured capacitance was not used. The fit is only for the “passive” nonlinearity of the conductance. The analyticity of the admittance only constrains $C(\omega)$ with $1/R(\omega)$. Aside from the mechanism under discussion, there should be no other correlation between the nonlinearity and the capacitance. This is clear from the data above 100 Hz (see Figure 3.1). The negligibly small nonlinearity leads only to the UDR-like capacitance despite the strong dispersion of $1/R(\omega)$.

4.3 Supporting Evidence

It should be noted that, in deriving the mechanism, specific properties of the ER fluid were not mentioned. Additionally, as discussed above, almost all reported

instances of NC involve; a dc bias, nonlinear I-V characteristics, and dispersion. The applicability of the proposed “passive” mechanism, therefore, should not be limited to the fluid. Unfortunately, the information reported in the literature is limited which prohibits a quantitative reanalysis in most cases. Sufficient data for such reanalysis, however, has been published for a ($H_2/H_2+2\% CO$) PEM fuel cell [4]. The low frequency NC of the fuel cell was attributed to the removal of contaminants (CO) from the electrode surface. Thus, the NC arises, not across the bulk electrolyte of the cell, but at the electrode interface.

The differential conductance and capacitance were taken from Figure 6 of reference [4]. The calculation of G_1 (from equation (4.9)) is more complicated in this case. For instance, the approximations that were employed to calculate $G_0 = \frac{I_{dc}}{V_{dc}}$ of the ER fluid are not justifiable for the fuel cell.

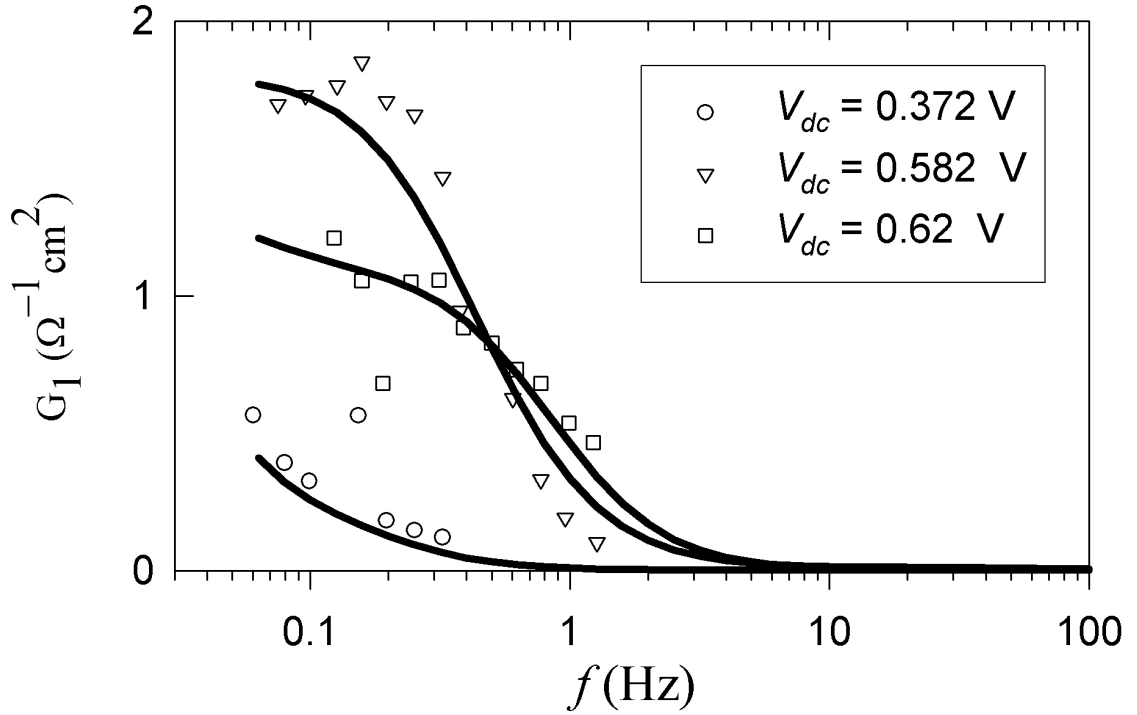


Figure 4.2. The nonlinearity of the fuel cell from Ref. [4]. Symbols represent data. Lines represent fits to two plasma relaxations.

Here, the current must be determined by integrating the conductance, *i.e.*,

$$I(\omega_1, V_{dc}) = \int_0^{V_{dc}} \frac{dV'}{R_{ac}(\omega_1, V')} . \quad (4.17)$$

Equation (4.17) is exact in the static limit yet may be a reasonable approximation at low frequencies. The voltage dependent conductance data was obtained from figure 9 of the reference, which displays information for $\omega_1/2\pi = 0.125$ Hz only. Two relaxations were used to fit the nonlinearity (lines in Figure 4.2). Fortunately, this single frequency current results in adequate fits for all frequencies at which the capacitance is negative.

The predicted NC (Figure 4.3) agrees with the data reasonably well considering the limited data reported. Note further that, like the ER fluid, the NC vanishes as G_1 tends toward zero.

The physical and chemical processes of fuel cells and ER fluids are very different. However, both exhibit NC which can be described by the model. It appears, therefore, that the mechanism is a general one.

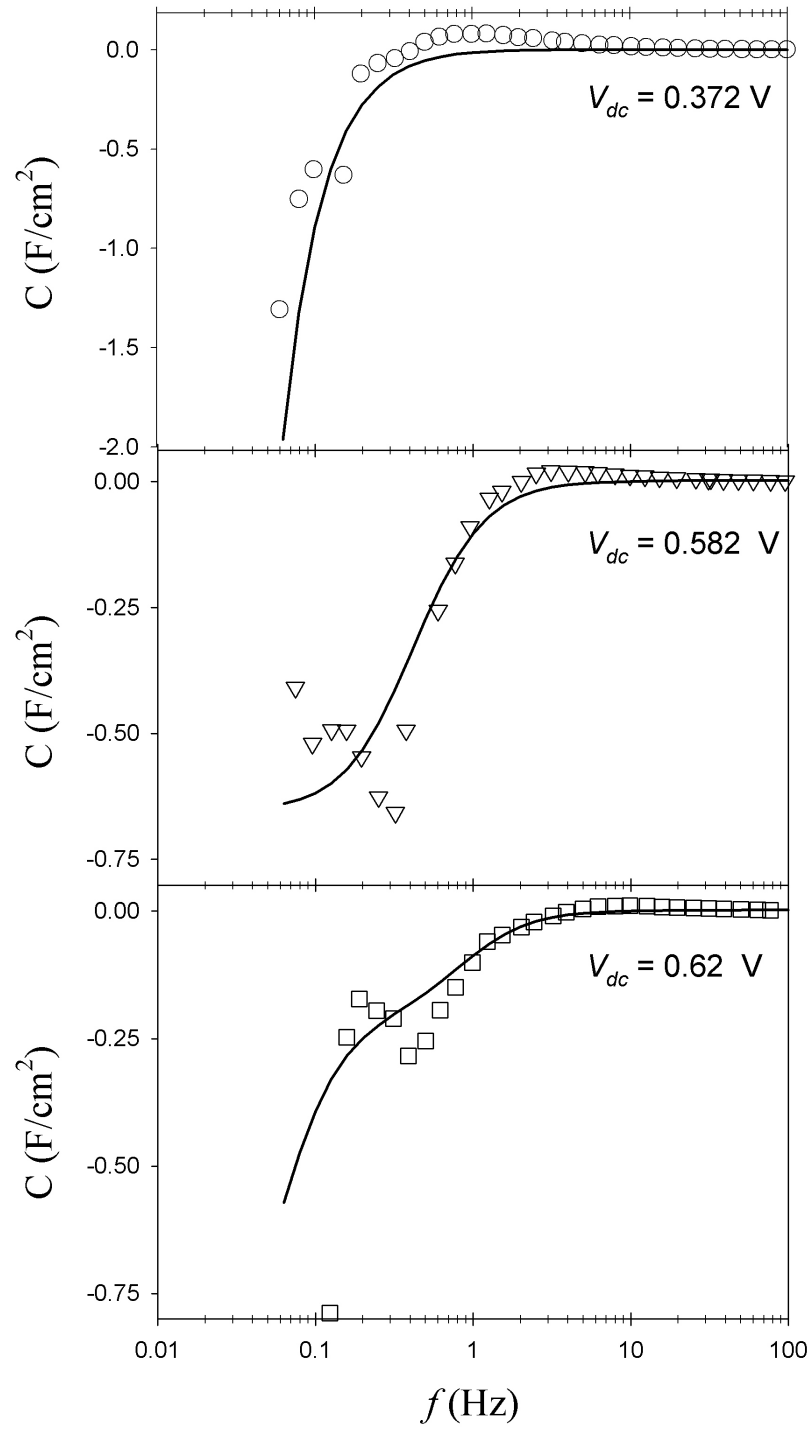


Figure 4.3. The capacitance of the fuel cell from Ref. [4]. Symbols represent data. Lines represent predictions from the mechanism.

4.4 Further Comments on the Dielectric Constant

In the previous chapter, it was argued that a mechanism based on electrode phenomena required an exceptionally large interfacial capacitance to account for the measured data. Furthermore, the thickness dependence data were inconsistent with what was expected from interfacial effects, but demonstrated that the NC arose in the bulk of the fluid. This played a significant role in concluding that the NC of the fluid was related to a negative dielectric constant. The mechanism presented here offers another tool to verify the bulk effect in the fluid. At low frequencies, a system consisting of an interface coupled to a bulk resistance and capacitance has a conductance of $G = \frac{1}{R_i + R_b}$,

where $R_{i,b}$ represent the resistance of the interface and bulk. In Chapter 3 it was argued that $R_b \gg R_i$. Physically, such a relationship seems reasonable since zero bias impedance data has determined the cell resistance to be larger than $1\text{G}\Omega$. It is hard to imagine an interfacial layer representing a significant fraction of such a large resistance, even if a bias is applied. The relatively small R_i cannot account for the large nonlinearity

(Figure 4.1a) of $\frac{dG}{dV} \sim \frac{1}{5} \text{ G}\Omega^{-1}/\text{V}$. That is, any small change in voltage will yield a change in conductance larger than any reasonable interfacial resistance. However, the large bulk resistance can account for such nonlinearity. Thus, it is clear that the NC arises due to the nonlinearity in the bulk of the fluid, further supporting the notion that the NC in the ER fluid is associated with a negative differential dielectric constant.

4.5 Chapter References

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Chapter 5: Concluding Remarks

The development of a mechanism that successfully predicts and describes the negative capacitance (NC) of the electrorheological (ER) fluid and other materials represents the culmination of this project. While NC has undergone limited study for decades, it remains relatively unknown despite being quite common. For the most part, the investigations have been restricted to individual materials. Very little work has been performed on NC as a general phenomenon. It is hoped that the results of this study will significantly enhance the scientific community's understanding of NC.

While generally accepted now, NC has been met with skepticism in the past. A great deal of care, therefore, has been placed on ensuring that the capacitance experiments measured the actual capacitance of the sample. The circuits were carefully calibrated with various resistor and capacitor combinations such that it can be conclusively stated that the phase angles detected during the experiments were a result of the sample, and thus, they represent a legitimate capacitive effect. This is supported by the agreement between the frequency and time domain experiments.

In some materials, the NC can be related to a negative differential dielectric constant. Essentially, in addition to a linear relationship between the *ac* current and voltage, the NC must arise in the bulk of the material. These conditions hold for the ER fluid in the small signal limit, and thus, the plasma-like NC of the fluid is associated with a negative differential dielectric constant. This, however, is not always the case. The fuel cell, which was discussed in Chapter 4, possesses an NC that originates at the electrode interface. In this situation, a dielectric constant cannot be connected to the NC.

Of foremost importance to this work is the impedance data demonstrating the low frequency NC of the ER fluid. This reveals that the fluid possesses a plasma-like NC, which is enhanced as an applied bias is increased (to a threshold bias). The conductance of the fluid was also shown to exhibit plasma-like behavior, even though it was masked in the original impedance data.

The frequency domain data was supplemented with results from time domain experiments. In addition to substantiating the frequency domain results, these measurements provided considerable insight regarding the nature of the observed dielectric behavior. Of significant interest was the observation of a negative transient current. This transient current was found to flow against the applied electric field for an extended period of time ($\gg 10^2$ s). Furthermore, the transient current was shown to result from the plasma-like nature of the fluid's admittance.

The NC of the ER fluid is the source of interesting charge flow behavior in general. Large amplitude *ac* voltage signals yield an off-phase current consisting of three loops when plotted against voltage. The direction that the loops are traced in time changes as the dielectric constant changes sign. Integration of this current with respect to time results in the charge accumulated across the sample, or polarization. The majority of the charge accumulated over one cycle is negative. This is reasonable but difficult to envision in the frequency domain. From the time domain perspective, the negative transient current carries charges in the direction opposite to that of a conventional dielectric. Therefore, at larger biases the polarization of the ER fluid is negative. All of these features are consistent with those expected from a material with a negative dielectric constant.

Pellets, made from the ER nanoparticles, exhibit dielectric behavior which is similar to that of the fluid. Silicone oil is clearly irrelevant to the NC, and the NC effect cannot be associated with the ER effect since large scale particle motion and rearrangement are restricted in the pellet. The effect is, however, closely connected to the moisture content of the pellet. Upon drying, a pellet subject to a bias exhibits a dispersion of the dielectric constant that closely resembles that of the pellet and fluid at zero bias. That is, the NC is suppressed and the behavior is largely UDR-like.

An early observation, which eventually aided in the development of the mechanism, was the enhancement of the NC in the ER systems by an increase in voltage, an increase in temperature, and an increase in moisture. An increase of all of these parameters results in an increase in the conductivity of the material. It was concluded that the conductivity is intimately related to the NC. Furthermore, the effect of moisture on the pellet suggests that the surface conductivity of the nanoparticles is the relevant parameter in the system. The relationship between the NC and the conductivity was later verified with the development of the mechanism, through which it was shown that the nonlinearity of the conductance is the key factor in determining the NC.

Of course, the most significant result to arise from this work was the general NC mechanism, which is applicable to many materials in addition to the ER fluid. The mechanism was developed by exploiting the features common to the many instances of NC reported in the literature. NC is typically observed in nonlinear materials with dispersion and in the presence of a *dc* bias. The *dc* bias and the nonlinearity combine to create a second term in the *ac* current when the material is subjected to a small *ac* excitation. The dispersive nature of the material often results in this current lagging

behind the excitation, which is the exact expression of a negative capacitance. Physically then, the NC is a result of the *dc* and *ac* signal mixing across a dispersive nonlinear material. In order to calculate this effect, one only needs knowledge of a material's nonlinearity.

The mechanism correctly describes the NC of both the ER fluid and the fuel cell discussed in Chapter 4. Clearly the predictions of the mechanism are insensitive to the exact nature of the NC in question since the two materials are vastly different. In addition, the NC of the fluid arises in the bulk of the material while the NC of the fuel cell occurs at the electrode interface. Therefore, the applicability of the mechanism appears to be quite general, and it is suggested to be valid for a wide range of NCs observed across a variety of materials. Negative capacitance is quite an abstract concept. However, in light of the mechanism, questions about the origin of NC in a particular material are now equivalent to asking why the material is dispersive and nonlinear. Dispersion and nonlinearity are much more tangible, as well as accessible, than NC itself. Thus, the new mechanism provides a significant simplification to the original problem. Furthermore, dispersion and nonlinearity can be attained through many microscopic processes. The early puzzle of the many physically distinct materials having similar manifestations of NC is, therefore, explained by the mechanism.